UNIVERSAL
LIBRARY

OU_154791

UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No. 544/R25E Accession No. 28511

Author Reddy, J.H.

Title Elementary Qualitative Analysis

This book should be returned on or before the date last marked below.

INTERNATIONAL CHEMICAL SERIES

LOUIS P. HAMMETT, PH.D., *Consulting Editor*

* * *

ELEMENTARY QUALITATIVE ANALYSIS

for College Students

The quality of the materials used in the manufacture of this book is governed by continued postwar shortages.

A SELECTION OF TITLES FROM THE

INTERNATIONAL CHEMICAL SERIES

LOUIS P. HAMMETT, PH.D., *Consulting Editor*

Amsden—
Physical Chemistry for Premedical Students

Arthur—
Lecture Demonstrations in General Chemistry

Arthur and Smith—
Semimicro Qualitative Analysis

Booth and Damerell—
Quantitative Analysis

Briscoe—
Structure and Properties of Matter

Coghill and Sturtevant—
An Introduction to the Preparation and Identification of Organic Compounds

Crist—
A Laboratory Course in General Chemistry

Daniels—
Mathematical Preparation for Physical Chemistry

Daniels, Mathews, and Williams—
Experimental Physical Chemistry

Desha—
Organic Chemistry

Dole—
Experimental and Theoretical Electrochemistry

Gibb—
Optical Methods of Chemical Analysis

Glasstone, Laidler, and Eyring—
The Theory of Rate Processes

Griffin—
Technical Methods of Analysis

Hamilton and Simpson—
Calculations of Quantitative Chemical Analysis

Hammett—
Physical Organic Chemistry
Solutions of Electrolytes

Henderson and Fernelius—
Inorganic Preparations

Huntress—
Problems in Organic Chemistry

Leighou—
Chemistry of Engineering Materials

Long and Anderson—
Chemical Calculations

Millard—
Physical Chemistry for Colleges

Moore—
History of Chemistry

Morton—
Laboratory Technique in Organic Chemistry
The Chemistry of Heterocyclic Compounds

Norris—
Experimental Organic Chemistry
The Principles of Organic Chemistry

Parr—
Analysis of Fuel, Gas, Water, and Lubricants

Reedy—
Elementary Qualitative Analysis
Theoretical Qualitative Analysis

Rieman, Neuss, and Naiman—
Quantitative Analysis

Robinson and Gilliland—
The Elements of Fractional Distillation

Schoch, Felsing, and Watt—
General Chemistry

Snell and Biffen—
Commercial Methods of Analysis

Steiner—
Introduction to Chemical Thermodynamics

Stillwell—
Crystal Chemistry

Stone, Dunn, and McCullough—
Experiments in General Chemistry

Thomas—
Colloid Chemistry

Timm—
General Chemistry
An Introduction to Chemistry

Watt—
Laboratory Experiments in General Chemistry and Qualitative Analysis

Williams and Homerberg—
Principles of Metallography

Woodman—
Food Analysis

ELEMENTARY QUALITATIVE ANALYSIS

for College Students

by J. H. Reedy
Associate Professor of Chemistry
in the University of Illinois

Third Edition
SEVENTH IMPRESSION

McGRAW-HILL BOOK COMPANY, Inc.
NEW YORK AND LONDON
1941

ELEMENTARY QUALITATIVE ANALYSIS

COPYRIGHT, 1924, 1932, 1941, BY THE
McGRAW-HILL BOOK COMPANY, INC.

PRINTED IN THE UNITED STATES OF AMERICA

*All rights reserved. This book, or
parts thereof, may not be reproduced
in any form without permission of
the publishers*

PREFACE TO THE THIRD EDITION

Since the publication of the second edition of this manual nine years ago, semimicro analysis has come into extended vogue. The most important feature of this new approach is the use of the centrifuge in speeding up the separation of precipitates. The principle of separation by centrifugation has now been found to be just as practicable for macro as for semimicro work, and it has been generally employed in this book in cases where the semimicro procedure is not feasible. Another notable advance is the more extended use of suction filtration.

On the chemical side, it has been the author's purpose to build procedures on facts within the range of the student's previous training. To this end, the new organic reagents have been avoided, notwithstanding their superior sensitiveness. The underlying purpose has been, not to set up mechanical procedures for identifying unknown materials, but to teach the reactions of general chemistry.

Several new procedures have been included, looking toward a shortening and simplification of certain tests. The new procedure for the Tin Subgroup has been found timesaving and reliable. The use of alcohol to sensitize the separations and tests in the Alkali Group also gives gratifying results. Particular effort has been made to lay down a definite procedure for the detection of anions—one that the student can follow easily and intelligently.

This volume is not the work of one man. The analytical staff at the University of Illinois has made many suggestions and criticisms. Particular thanks are extended to Dr. B. C. Marklein of Lafayette College for reading the manuscript, and to Dr. A. R. Hanke of the Kansas State Agricultural and Mechanical College, who did most of the experimental work on the new Tin Subgroup procedure.

J. H. Reedy.

The W. A. Noyes Laboratory,
University of Illinois,
January, 1941.

PREFACE TO THE FIRST EDITION

This book is an attempt to put in printed form the system of laboratory and quiz room instruction that has been developed during recent years in the elementary courses in Qualitative Analysis at the University of Illinois. It presumes that the student has had the equivalent of not less than five semester hours of college chemistry, and that he is able to follow laboratory directions with a reduced amount of oversight on the part of the instructor.

The fundamental purpose in the compilation of this manual has been to enable the student to know at all times exactly what he is doing. The notion, occasionally heard, that the function of a course in qualitative analysis is to "teach a student to follow directions" is rejected, not only because it is a purely mechanical approach to the subject, but also because it is perversive of the best development of the student. There is too great a tendency, even in the best of our teaching, for the student gradually to accept the attitude that analytical procedures are more or less unintelligible processes, which, if carefully followed, will in the end tell what the ingredients of a substance are. In order to anticipate and, as far as possible, prevent such an attitude, the preliminary experiments have been designed to set forth in simple, independent tests the fundamental reactions involved in analytical work; and lists of simple exercises have been included to direct attention to these reactions. Theoretical discussions to explain results are given as notes, placed as close to the experimental directions as possible.

The endeavor has been made to put nothing in this book that the elementary student might not be expected to understand. The notes and general discussions have been prepared with great care, and the writer feels that the instructor should not allow the students to slight this very important part of the work. Students should be given to understand at the beginning that they will be held accountable for the notes on all the procedures assigned by the instructor, and the latter should not fail on his part to quiz them constantly on these discussions.

A number of paragraphs have been included that may be omitted at the discretion of the instructor, without in any way involving the continuity of the analytical procedure. Most of these have to do with the detection of the less common ions, and a few of them require more or less dangerous reagents. Such paragraphs have been marked with asterisks.

The procedures in this manual have been chosen with a view to their reliability in the hands of elementary students. For the most part, they are methods found in other manuals, but reproduced here with many modifications or adaptations in favor of the beginning student. Some of the procedures are new to elementary manuals. Method A for the Tin Subgroup has been adapted from the very satisfactory quantitative procedure of Clarke for separating tin from arsenic and antimony, and has been found at the University of Illinois to give better results than other procedures. A new procedure for the analysis of the Iron Subgroup in the presence of phosphates and oxalates is also included. The general scheme for the detection of the anions is, with certain changes, the one worked out by this writer and published in the seventh edition of W. A. Noyes's "Qualitative Analysis" (Henry Holt and Company). In two cases it has been felt worth while to give alternative methods. The method of A. A. Noyes has been included as an alternate procedure in the Tin Subgroup, and the Gooch-Browning method for the separation of Ca^{++} from Sr^{++} by means of potassium ferrocyanide as an alternate procedure in Cation Group IV.

The writer is glad to acknowledge his debt to the large group of instructors and assistants at the University of Illinois who have collaborated so enthusiastically in trying out the new procedures; to Dr. R. W. Hufferd of DePauw University for suggesting the use of the Vogel test for Co^{++}; and particularly to Drs. T. E. Phipps and L. F. Yntema of the University of Illinois for criticism of the manuscript and for many suggestions that have been incorporated in these pages.

J. H. REEDY.

URBANA, ILLINOIS,
August, 1924.

CONTENTS

PAGE

PREFACE TO THE THIRD EDITION v

PREFACE TO THE FIRST EDITION vii

INTRODUCTION 1
  Macroanalysis and Microanalysis 2
  Terms and Operations Used in Chemical Analysis 3

PART I. PRELIMINARY LABORATORY WORK

CHECKING IN; PREPARATION OF WASH BOTTLE AND OTHER EQUIPMENT 11

PART II. DETECTION OF THE IONS OF THE METALS

GROUPS OF THE METALLIC IONS (Cations) 14
DETECTION OF CATION GROUPS IN A SOLUTION 14
  Preliminary Experiments 14
  Analysis 17

GROUP I—THE HYDROCHLORIC ACID GROUP 19
  Preliminary Experiments 19
  Analysis 22

GROUP II—THE HYDROGEN SULFIDE GROUP 23
  Preliminary Experiments 23
  Analysis 34

GROUP III—THE AMMONIUM SULFIDE GROUP 44
  Preliminary Experiments 45
  Analysis 54

GROUP IV—THE AMMONIUM CARBONATE GROUP 65
  Preliminary Experiments 65
  Analysis 69

GROUP V—THE SOLUBLE GROUP 73
  Preliminary Experiments 74
  Analysis 78

PART III. DETECTION OF THE IONS OF THE NON-METALS

Page
Anion Groups and Group Reagents 82
Anion Group I 83
Anion Group II 88
Anion Group III 90
Anion Group IV 96
Anion Group V 99
Anion Group VI 101
Systematic Analysis of Anions 102
  Solutions (Case I) 103
  Solids (Case II) 108
  Analysis of Anion Group I 112
  Analysis of Anion Group II 115
  Analysis of Anion Group III 118
  Analysis of Anion Group IV 123
  Analysis of Anion Group V 125
  Analysis of Anion Group VI 127

PART IV. SYSTEMATIC ANALYSIS

Removal of Organic Matter 130
Dissolving the Substance 131
  Solids, Not Metals or Alloys 131
  Metals and Alloys 131
  Ores and Insoluble Salts 133

APPENDIX

Laboratory Records 137
Unknowns 139
Electromotive Series 140
Reagents 141
Laboratory Outfit 146
Table of Solubilities 148
Periodic System 152

Index 153

ELEMENTARY QUALITATIVE ANALYSIS

INTRODUCTION

The purpose of qualitative analysis is to ascertain the elements or groups (*i.e.*, radicals) which are present in a given substance. The examination should be quantitative to the extent that the student should distinguish between the main components of the material which are present in relatively large amounts, and those constituents which are present in small quantity, perhaps only as traces.

Since most of the processes involved in ordinary qualitative procedure are reactions between solutions, the actual tests as usually carried out are tests for the ions and not for the elements themselves. Metals are usually present in a solution as cations, bearing charges of positive electricity, *e.g.*, sodium as Na^+, or iron as Fe^{+++}. Occasionally, however, metals appear in complex anions, as iron in ferrocyanides, in which the metal occurs in the complex anion, $Fe(CN)_6^{----}$. The non-metals, with the exception of hydrogen in acids and nitrogen in the ammonium group, are uniformly present in anion groups.

In general, a metallic ion must be separated from other metallic ions before a conclusive test may be made for its presence. This separation is carried out in a systematic way, first by precipitating the cations in groups, and later by separating the groups into their component ions. After a solution containing the ion in question, free from all interfering ions, has been obtained, the *specific test* for the ion is made. If this test is not sufficiently sensitive, or if it is obscured by failure to have the solution free from interfering substances, a confirmatory test is made. It follows from this that a *confirmatory test* should either be more delicate than the first test or else be free from interferences by the other substances present in the solution. Later in the course it will be pointed out how, when a test appears weak and indecisive, it may be accurately interpreted by comparison with a *blank test* and a *control test.* In the former, the test reagent is applied to a liquid (usually water) free from the ion in question; in the second, the test is made on a very dilute solution containing the ion. By comparing the actual test with the blank and control tests, the presence of the ion which is being tested for may be decided with certainty.

For the most part, the separations in analytical chemistry are made by converting the ions of the solution into compounds which have wide differences in solubility. For example, Ba^{++} may be separated from Cu^{++} by adding a solution containing the SO_4^{--} anion. It may be assumed that there is a tendency for both $BaSO_4$ and $CuSO_4$ molecules to form in the solution; but since the former is insoluble in water, while the latter is soluble, only the Ba^{++} is precipitated. It follows, then, that analytical procedures are based largely, if not wholly, on differences in solubility, and the student should learn to interpret these procedures in the light of solubility relationships. Frequent reference will be made to the Table of Solubilities on pages 148–151.

MACROANALYSIS AND MICROANALYSIS

Formerly chemical analysis was carried out on a "macro" scale, using considerable amounts of material. The weight of substance used for an analysis would range from 0.5 to 1 gram, and the volume of the solution employed would approximate 100 ml., or even more. Recently, "micro" methods have been developed, using drops or milligrams where milliliters or grams were used on the macro scale. As a compromise between two extremes, "semimicro" methods have come into vogue. The chemistry involved in semimicro methods is the same as that used in macro methods, but specialized technique is used to avoid losses of materials.

Semimicro methods are not more sensitive than macro methods. On the other hand, using the same reagents, they are apt to be less sensitive, owing to losses in filtration and washing. The advantage of semimicro methods lies in saving time in making evaporations, filtrations, and so forth.

Microanalysis, as now developed, is far more sensitive than macro or semimicro methods. This follows from the use of new reagents, which are highly specific in their reactions. These reagents are organic, for the most part, and an understanding of the chemistry involved is beyond the ability of elementary students. Furthermore, very elaborate and clever manipulation is called for, in order to prevent loss of material and to further sensitize the reactions.

TERMS AND OPERATIONS USED IN CHEMICAL ANALYSIS

Solutions.—Most of the operations of qualitative analysis are "wet" reactions, carried out in solution. A *solution* is thought of as being a physicochemical union of a *solvent* (usually a liquid) and a *solute*, which may be solid, liquid, or gas. The solvent is usually present in excess.

Reactions.—Separations in chemical analysis are carried out by subjecting the substance to various treatments, such as the addition of chemicals, the application of heat, and so forth. The results of these treatments are called *reactions*. For example, when hydrochloric acid is added to a solution of silver nitrate, a white solid is formed; or, when an ammonium salt is warmed with caustic soda, a gas (ammonia) is evolved. Note that reactions are physical phenomena which register on our senses of sight, touch, smell and, occasionally, taste and hearing. The materials taking part in a reaction are called the *reactants;* the materials formed are called the *products*. The algebraic expression representing the weight relationship between reactants and products is the *equation*. When a reagent is added for the purpose of producing a precipitate, it is called the *precipitant*. Reagents may be further classified by some particular property, an oxidizing agent, dehydrating agent, catalytic agent, etc.

Precipitation.—The formation of a solid by the interaction between two reagents is called *precipitation*. Slight or finely divided precipitates may appear as a turbidity. Sometimes the size of the particles is so minute that the precipitate will pass through the pores of the filter paper or will even be invisible to the eye. These invisible precipitates are called *sols*. Precipitates are usually described as crystalline, pulverulent, curdy, or colloidal. The latter are gummy and tend to plug the pores of the filter paper. In many cases, precipitates may be changed from colloidal toward the crystalline form by proper treatment. (See Digestion.)

Mixing.—The precipitates obtained when solutions are "dumped" together are frequently colloidal and hard to filter. Reagents should be added slowly and mixed with the solution by stirring or shaking. A solution should never be mixed by shaking it against the thumb. Such a procedure is hard on both thumb and solution.

Filtration.—The most common method for separating a precipitate from a liquid is filtration, in which the liquid passes through a medium which will retain the precipitate. The usual medium for this purpose is "filter paper"—paper from which all mineral matter has been removed by washing with acids. Asbestos, glass wool, and other materials are used for solutions which attack paper.

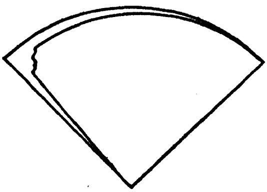
FIG. 1.—Folded filter paper.

Filtration on a Macro Scale.—As ordinarily carried out, a filter paper is folded twice (Fig. 1), usually staggering the quarters very slightly, so as to make the central angle a little greater than 90 deg. In this way the upper angles of the paper meet the funnel " a little too soon," providing a close fit so that air cannot pass between the paper and the glass. If air channels are left, it will not be possible to maintain an unbroken column of filtrate in the stem of the funnel. The weight of this column acts as a mild suction and thereby hastens filtration.

Spattering should be avoided, not only to prevent loss of materials but also for the sake of cleanliness. Solutions should be poured down a stirring rod, and the stem of the funnel should be in contact with the side of the beaker or dish. (See Fig. 2.) Suction filtration is not successful with colloidal precipitates. The precipitates plug the pores of the paper, so that the solution passes slowly, if at all. Gelatinous precipitates are best filtered through fluted papers, which afford a maximum of filtering surface. Suction with fluted papers is not possible.

Filtration on a Micro Scale.—In dealing with small quantities of solution and precipitate, care must be taken that none of either is lost. Small filters are used, and the filtrate is received in a small test tube. The setup in Fig. 3 is useful in such a case. The outfit consists of an ordinary 250-ml. bottle of the wide-neck type. It is closed loosely by a large two-holed rubber stopper, carrying a 4-cm. funnel and an elbow tube. By means of a slotted cork or rubber stopper, a small test tube is attached to the stem of the funnel. The elbow is connected to the air pump or vacuum system. The suction can be regulated by pressing the stopper against the mouth of the bottle.

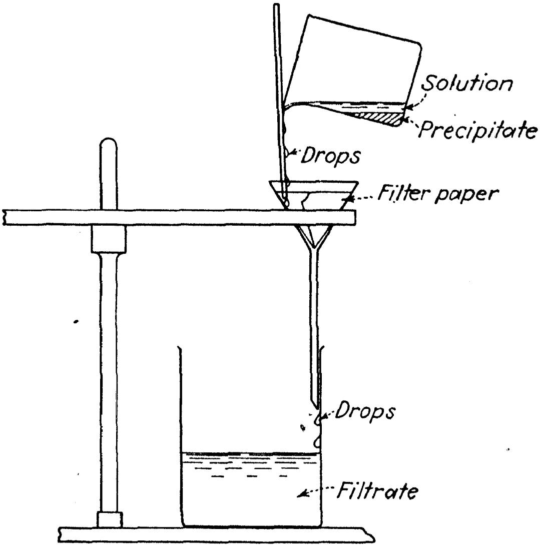

FIG. 2.—Filtration (macro).

Decantation.—If the precipitate is heavy and settles well, separation may be effected simply by pouring off the liquid. A single decantation never gives a complete separation, for a considerable quantity of the solution is retained by the precipitate. The precipitate must be mixed with a small volume of wash solution, and, after resettling, the decantation is repeated. Sometimes two or more operations are necessary to wash the residue sufficiently.

The centrifuge is very effective in settling suspended particles.

Some precipitates are light and go back into suspension upon slight agitation. In this case, the liquid may be withdrawn by means of a pipette. Care must be taken that the tip of the pipette does not reach the surface of the precipitate, so as to disturb it. Furthermore, in using bulb pipettes, the bulb should be compressed before inserting the tip in the solution. There is no better stirring agent than a stream of air bubbles.

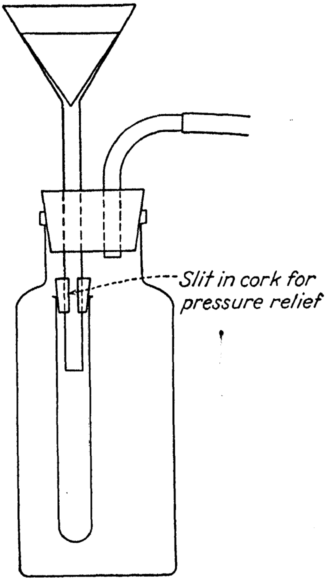

Fig. 3.—Filtration on a micro scale, using suction.

In most decantations, it is better to pass the decantate through a filter, so as to prevent the loss of any of the precipitate and the introduction into the solution of complicating substances.

The Centrifuge.—The sedimentation of precipitates is hastened by whirling in machines called *centrifuges* (Fig. 4). Precipitates that ordinarily require 1 hr. for settling, *e.g.*, $Al(OH)_3$, may be thrown down in a compact mass in a few minutes. The liquid separated by means of a centrifuge is sometimes called the *centrifugate*.

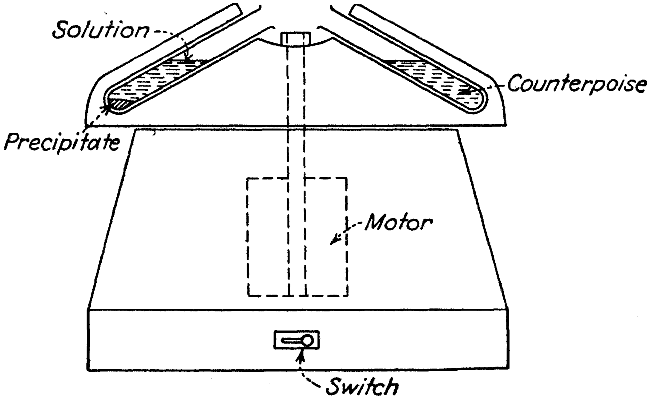

Fig. 4.—Diagram of centrifuge.

When several students use the same centrifuge, each student should stand by until his operation is complete. Otherwise an exchange of tubes may occur. In all cases, a tube should be counterpoised by placing just opposite it in the head a tube containing an equal amount of water. This is necessary to prevent vibrations, which are destructive to the motor. A cracked tube should never be centrifuged. The outside of the tube should be clean and dry, so as to save the thimbles or containers from corrosion. Accidents should be reported promptly to the instructor, sò that he can take steps to prevent permanent injury to the machine.

Digestion.—Precipitates filter better if they are allowed to remain in the "mother solution" a while before introducing them on the filter. During this "aging," smaller particles redissolve and reappear as larger particles. Digestion is often combined with heating.

Effect of Electrolytes.—The presence of an electrolyte tends to make colloids filter better, and conversely, when the electrolyte is washed out, the precipitate tends to "go back into solution" and "run through the filter." The electrolytes used to coagulate precipitates in this way are usually volatile ones, so that they can be removed by evaporation or ignition. HCl, NH_4Cl, NH_4NO_3, and $NH_4C_2H_3O_2$ are the ones most commonly used.

Washing of Precipitates.—The impurities adsorbed by a precipitate cannot be removed by simple draining. They must be washed out (or "extracted") by means of a liquid that will dissolve them, but not the precipitate.

If the precipitate has been separated by filtration, the wash solution is applied directly to the filter paper in the funnel. A small portion of the solution is added at a time, and the precipitate is allowed to drain before a second portion is introduced. If the precipitate has been thrown down by centrifugation, the mother liquor is poured off, and a small amount of the wash solution is added. Any lumps in the precipitate are then broken down by stirring or shaking, and the mixture is again centrifuged. The latter method is called "washing by decantation."

Colloidal precipitates are particularly hard to wash, for they have the power of adsorbing the dissolved matter very tenaciously. In such cases the precipitate is washed, not with water, but with a solution of an electrolyte, which will displace the adsorbed impurity.

Heating Solutions.—The full flame of the ordinary Bunsen burner is too powerful for heating solutions in small test tubes. Large bubbles form and the whole of the solution may be thrown out of the tube. If the tube is held an inch or more above the flame and constantly moved in a circular fashion, violent ebullition may be avoided. (A safer procedure is to use the flame of a micro burner, or, better still, the solution may be heated in a water bath. This consists of a beaker of water, kept near its boiling point by means of the regulated flame of a Bunsen burner. In semimicro work, this bath should be kept in operation throughout the laboratory period.)

Precipitation by Hydrogen Sulfide.—The procedure differs, depending on the amount of solution to be treated.

Macro Procedure.—Precipitation in solutions of 25 to 100 ml. are carried out in the apparatus shown in Fig. 5. The outfit consists of a 250- or 300-ml. Erlenmeyer flask, fitted with a one-holed rubber stopper carrying a glass tube bent at a convenient angle for making connection with the gas supply. This tube should not extend into the solution, but just through the stopper. Connection to the H_2S cock is made by a piece of flexible rubber tubing. After turning on the gas, the stopper is loosened for a moment so as to displace the air, and then is pressed tightly into place. Occasional shaking (by rotating the flask horizontally) will hasten precipitation. If the solution should accidentally be thrown against the stopper and tube, they should be thoroughly cleaned before being used again.

Hydrogen sulfide should not be bubbled through a solution in an open vessel, except when working on a micro scale. This gas vitiates the air in the room and spoils results in other experiments. More than that, H_2S *is poisonous*, and its presence in quantity may cause collapse or even death.

When volumes of 5 to 25 ml. of a solution are to be saturated with H_2S, a 125-ml. flask is used instead of the 250-ml. flask, and greater care must be taken in shaking, so as not to introduce the solution into the H_2S delivery lines.

Micro Procedure.—When small volumes of solution are to be treated with H_2S, a form of bubbling system is used (Fig. 6). The gas is introduced as small bubbles through a capillary tube, since in this form the gas is dissolved more rapidly. Further-

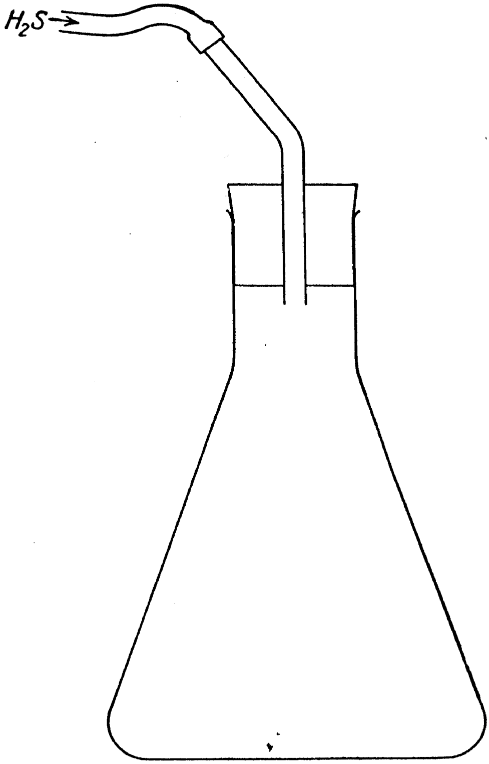

Fig. 5.—Precipitation by H_2S (macro method).

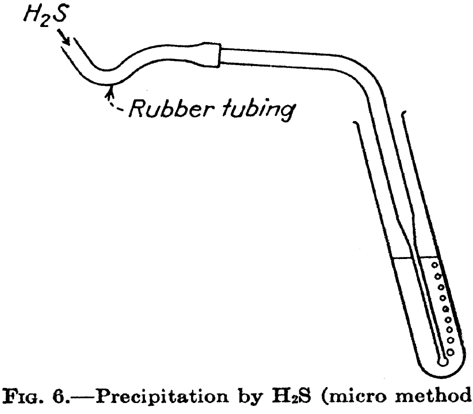

Fig. 6.—Precipitation by H_2S (micro method).

more, large bubbles might push a solution out of a narrow test tube. If the capillary is too small, a booster in the form of a rubber bulb must be introduced into the gas line to force the gas through the tube. A little of the gas escapes unabsorbed, but the amount is small, and the pollution of the air is never large enough to be dangerous.

Ignition.—Precipitates or residues are sometimes heated to expel certain volatile constituents. This "dry heating" is called *ignition.* The chemical use of the term is quite different from the ordinary one, which means "setting fire to." Ignition in chemical procedures is carried out by applying the heat beneath the vessel containing the substance, and *not within it.*

PART I

PRELIMINARY LABORATORY WORK

(1) **"Checking In."**—After a desk has been assigned, obtain the key or combination from the storeroom. Check the apparatus in the desk against the list furnished you. In case any articles are broken or missing, report the fact to the laboratory instructor, who will issue an order to the storekeeper to furnish them. Then sign the apparatus list and turn it in at the storeroom.

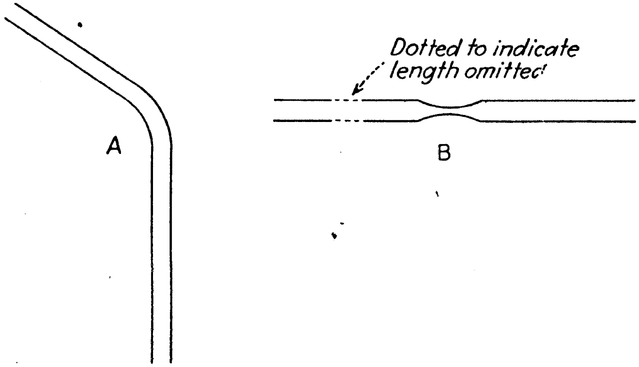

FIG. 7.—Mouthpiece and delivery tube for wash bottle.

Keep the outfit in the desk in as orderly condition as possible.

Wash all glassware as it is returned to the cupboard, so that it will be ready for instant use when needed.

Replace any broken apparatus by purchases from the storeroom, thereby keeping a complete outfit in the desk.

(2) **Preparation of a Wash Bottle.**—Prepare a wash bottle according to the following directions: Fit a 300-ml. Erlenmeyer flask with a two-holed rubber stopper. To make the mouthpiece *A* (Fig. 7), use a flat, luminous flame[1] to make a bend of about

---

[1] All bends should be made with the flat, luminous flame, formed by using the wing top and adjusting the air holes at the base of the burner.

120 deg. in the middle of a piece of glass tubing about 12 cm. long. For the delivery tube *B*, take another piece about 30 cm. long and heat it about 5 cm. from one end in the colorless Bunsen flame, rotating it constantly until it softens. Remove it from the flame and pull the ends apart very slowly, so as to reduce the size of the heated portion, as shown in *B* (Fig. 7). After the tube has cooled, make a scratch with a file (be careful not to crush the tube) at the narrowest part and break. Next, bend the tube about 3 or 4 cm. from the tip to an angle of 60 deg., again using the flat luminous flame. Finally, make a bend of about 160 deg. about 5 cm. from the other end. Fire-polish the ends of all the pieces by heating them in the Bunsen flame until the glass just begins to soften, being careful not to close the jet of the nozzle by melting together the thin walls of glass. After cooling, moisten the tubes with water, and insert them in the holes of the rubber stopper. The stopper will easily pass around the slight bend in the delivery tube, if the tube is wet. The assembled bottle is shown in Fig. 8.

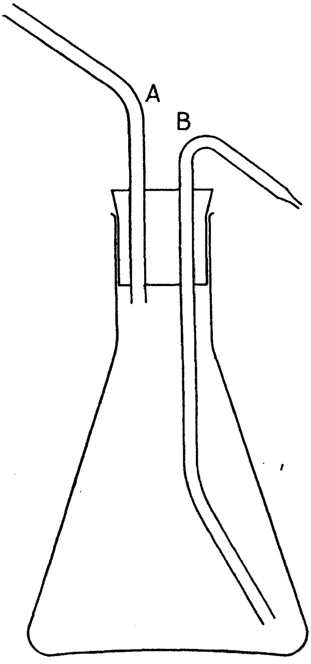

FIG. 8.—Wash bottle (assembled).

Rinse the bottle once with distilled water before filling. *Use distilled water sparingly.* The following are the more important procedures in which distilled water is used:

1. Rinsing apparatus (after washing with tap water).
2. Washing precipitates.
3. Diluting solutions.

(3) Other Equipment.—Prepare six stirring rods—two 10 cm. long, two 12 cm. long, and two 15 cm. long. Make these from glass rods about 3 mm. in diameter, so that they may be used in small test tubes. Heat the ends of these rods in the Bunsen flame until they are rounded, so that they cannot scratch the sides of the beakers and test tubes with which they are used. In addition to the stirring rods, make two glass fibers, by heating glass rods in a large flame and pulling them while hot down to a large fiber. (Instructions.) (See Fig. 9.) These fibers are very useful, although fragile. Store them in a small box or a large test tube to protect them from breakage.

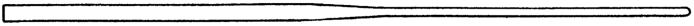

Fig. 9.—Stirring rod (micro).

Fig. 10.—Pipette.

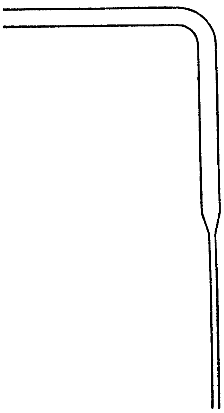

Fig. 11.—H_2S delivery tube (micro).

Prepare at least six pipettes by drawing capillary tips on pieces of glass tubing. (Instructions.) The tips should be about 10 cm. long, and the body should be about 20 cm. long. (See Fig. 10.) The capillary tips should be drawn as heavy as possible, so as to prevent easy breakage.

Make two or more delivery tubes for use in precipitations with hydrogen sulfide. (See Fig. 11.) Also make two elbows from pieces of glass tubing about 12 cm. long. One of these should have an angle of 90 deg., and the other of about 135 deg. Fire-polish the ends by heating in a Bunsen flame to a softening temperature.

Make up the apparatus for suction filtration on a semimicro scale. (See Fig. 3, page 6.)

PART II

DETECTION OF THE IONS OF THE METALS

GROUPS OF THE METALLIC IONS (CATIONS)

Systematic analysis of a solution for metallic ions consists, as a first step, in dividing the ions up into groups, and, as a second step, in separating the groups into their individual members. The reagents used in precipitating these groups are known as *group reagents.* These groups, with their group reagents and membership, are as follows:

Group	Name	Reagent	Membership
I	Hydrochloric Acid Group	Dilute HCl	Pb^{++}, Ag^{+}, Hg_2^{++}
II	Hydrogen Sulfide Group	H_2S (+ dilute HCl)	(*a*) Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++} (*b*) As^{+++}, Sb^{+++}, Sn^{++}, Sn^{++++}
III	Ammonium Sulfide Group	$(NH_4)_2S$ (or $NH_4OH + H_2S$)	(*a*) Al^{+++}, Cr^{+++}, Zn^{++} (*b*) Mn^{++}, $Fe^{++} - Fe^{+++}$, Co^{++}, Ni^{++}
IV	Ammonium Carbonate Group	$(NH_4)_2CO_3$	Ba^{++}, Sr^{++}, Ca^{++}
V	Soluble Group	None	Na^{+}, K^{+}, NH_4^{+}, Mg^{++}

Note.—Lead occurs in both Group I and Group II. Its presence in the latter group is due to a slight solubility of its chloride in water, with the result that its precipitation in Group I is not complete. Mercury also occurs in Groups I and II, but for a different reason, *viz.*, mercury forms two cations: mercurous, Hg_2^{++}, and mercuric, Hg^{++}; the chloride of the first is insoluble in water, while the chloride of the second is soluble. Consequently, they fall into different groups.

DETECTION OF THE CATION GROUPS PRESENT IN A SOLUTION

PRELIMINARY EXPERIMENTS

Note.—In performing the experiments in this course, the student should keep a concise and intelligible record of the results of each experiment.

For his guidance, questions to be answered are indicated by (?), equations to be written by (E), references to be consulted by (R), and special instructions in technique by (Instructions). These notes should be made as the experiment progresses and not at the end of the hour or outside the laboratory. The student should be encouraged to bring his textbook to the laboratory for use as a reference. See Appendix, pages 137, 138, for suggested forms of records.

(4) **Group I.**—Use $AgNO_3$ solution as representative of this group. Place 1 or 2 drops of this solution in a test tube, dilute with 1 ml. of water, and add dilute HCl dropwise, with shaking, until precipitation is complete. Filter or centrifuge, and test for the completeness of the precipitation by adding 1 drop of HCl to the filtrate or centrifugate. If more AgCl forms, repeat the filtration or centrifugation. Place the solution in a 50-ml. Erlenmeyer flask and saturate it with H_2S. From the result infer whether AgCl is soluble in water or not (?).

Note.—H_2S is a very sensitive test for the presence of Ag compounds. If AgCl were appreciably soluble in water, a brown color or precipitate would appear at this point.

(5) **Group II.**—Use $Hg(NO_3)_2$ solution as representative of this group. Dilute 1 drop of this solution to 4 ml. in a 50-ml. Erlenmeyer flask and add 4 drops of dilute HCl. Saturate the solution with H_2S, heat in the water bath, and decant or filter. After proving that precipitation is complete by adding 4 ml. of water and resaturating with H_2S, add NH_4OH to alkalinity (litmus test) and saturate with H_2S (?).

(6) **Group III.**—Use $Zn(NO_3)_2$ solution as representative of this group. Dilute 1 drop to 4 ml. and add 4 drops of dilute HCl (?). Saturate with H_2S (?). Now add NH_4OH with shaking until 1 drop of the solution on a stirring rod will turn red litmus blue. Saturate again with H_2S (?). After testing for completeness of the precipitation, add $(NH_4)_2CO_3$ solution to the filtrate (?).

(7) **Group IV.**—Use $CaCl_2$ solution as representative of this group. Dilute 1 drop to 4 ml., add 4 drops of dilute HCl (?), saturate with H_2S (?), add NH_4OH in excess (litmus test), resaturate with H_2S (?), and add 1 or 2 drops of $(NH_4)_2CO_3$. If a precipitate does not form at once, heat the mixture almost to boiling and let stand for ½ hr.

(8) **Group V.**—Use $Mg(NO_3)_2$ solution as representative of this group. Dilute 1 drop to 4 ml., add 4 drops of dilute HCl (?), saturate with H_2S (?), add NH_4OH to alkalinity, resaturate with H_2S (?), and add $(NH_4)_2CO_3$ (?). Define Group V (?).

Dilute 1 drop of $Mg(NO_3)_2$ to 2 ml. and add Na_2CO_3 solution (?). Would it be correct to say that $MgCO_3$ is soluble in water? To the mixture add 0.5 ml. of NH_4Cl and shake well (?). Why did not $MgCO_3$ form in the preceding test?

(9) **Effect of Incomplete Precipitation.**—Try the following experiments: $AgNO_3$ solution + H_2S (?), $Hg(NO_3)_2$ solution + NH_4OH + H_2S (?), $Zn(NO_3)_2$ solution + $(NH_4)_2CO_3$ (?). What would be the result if each of these cations was not completely precipitated in its own group?

Exercises[1]

1. Name the group reagent for each of the first four cation groups.
2. What is a test for completeness of precipitation?
3. Name three solutions besides HCl that might be used to precipitate AgCl from $AgNO_3$ solution.
4. A student reported Groups III and IV in a "group unknown" containing only $Zn(NO_3)_2$. Point out the error in his technique.
5. Suppose four portions of a "group unknown" are tested, each by one of the group reagents. If the unknown contained mercurous nitrate, $Hg_2(NO_3)_2$, what groups would be reported? (In case of uncertainty, try these tests.)
6. Fill in the blanks in the following sentences with the proper word, "soluble" or "insoluble."

AgCl is..................in water.
HgS is..................in water,....................in dilute acids.
ZnS is..................in water,....................in dilute acids, ...in NH_4OH.
$CaCO_3$ is..................in water,....................in water containing ammonium salts.

---

[1] The exercises at the end of each set of preliminary experiments are intended to be used in testing how much the student is getting out of his laboratory work. The questions are easy, and the student who has done his work faithfully and intelligently should have no trouble with them. An excellent plan is to give each student an informal quiz before issuing to him an unknown for analysis. A blackboard should be available in the laboratory for equations and calculations. Besides the laboratory tests, the questions should be helpful in review for the more formal examinations in the course.

$MgCO_3$ is................in water,.....................in water containing ammonium salts.

All nitrates in the above experiments appear to be............in water.

7. What is the meaning of the following symbols used in this book: (?), (E), (R), (Instructions)?

ANALYSIS

(10) Group I.—A 0.5-ml. portion should be sufficient for an analysis, if the unknowns are made up of the concentrated solutions proposed in the Appendix (pages 141–146). Dilute with about 2 ml. of water and disregard any precipitate that may form during dilution. Add exactly 4 drops of dilute HCl and stir the mixture thoroughly. If a precipitate forms, Group I is indicated. Settle the precipitate (by standing or centrifugation), and add 1 drop of dilute HCl to the clear solution at the top of the mixture. If more precipitate forms, discard the experiment and start again, using a smaller sample of unknown.

Pour off the supernatant solution and wash the precipitate by adding 1 ml. of cold water containing 1 drop of dilute HCl and then centrifuging and decanting the clear solution. Wash again, using 1 ml. of cold water. Add the washings to the first decantate and reserve for **(11)**. A final residue, insoluble in water and dilute HCl, is proof of the presence of Group I.

Notes.—1. The amount of dilute HCl used must not exceed 4 drops. If larger amounts are used the acidity will be too high to permit the complete precipitation of Group II by H_2S.

2. Bi^{+++} and Sb^{+++} (members of Group II) may form precipitates upon dilution, but these precipitates are redissolved upon washing with dilute HCl.

(11) Group II.—Transfer the decantate from Group I to a 50-ml. Erlenmeyer flask and saturate with H_2S. A precipitate indicates the presence of Group II. Filter or centrifuge, and test for completeness of the precipitation by resaturating the solution with H_2S. Wash the precipitate with a little warm water and reserve filtrate for **(12)**.

Note.—The failure to remove Group II ions completely is apt to lead the student to report Group III as present, which group may not be present at all.

(12) Group III.—To the acid filtrate from (**11**) add NH_4OH to alkaline reaction (litmus test) and saturate with H_2S. A precipitate indicates the presence of Group III. Centrifuge or filter, wash the precipitate, and reserve the filtrate for (**13**).

Note.—If the solution were not made alkaline with NH_4OH, Group III cations would be carried into Group IV, where they would give a false test for that group.

(13) Group IV.—Acidify the filtrate from (**12**) with dilute HCl and concentrate to 3 ml. by boiling in a casserole. Filter, if a precipitate (sulfur) appears. Add NH_4OH to alkaline reaction and heat almost to boiling in the water bath. Add $(NH_4)_2CO_3$ until precipitation is complete. Let the mixture stand at least 15 min. before deciding that no precipitate has formed. A precipitate indicates Group IV.

Note.—The precipitates of Group IV may form slowly. Heat and the presence of electrolytes favor their formation.

(14) Group V.—Since there is no group reagent for Group V, no further tests need be made, and no report on the presence or absence of this group need be given.

TABLE I.—SEPARATION OF CATION GROUPS

<table>
<tr><td colspan="5">(10)[1] Dilute 0.5 ml. of the unknown solution to 2 ml. and add 4 drops of dilute HCl. Filter or centrifuge, wash precipitate.</td></tr>
<tr><td rowspan="4">Precipitate:
Group I
(as chlorides).
See Table II.</td><td colspan="4">(11) Filtrate: Saturate with H_2S. Filter, wash precipitate.</td></tr>
<tr><td rowspan="3">Precipitate:
Group II
(as sulfides).
See Table III.</td><td colspan="3">(12) Filtrate: Add $NH_4OH + H_2S$. Filter, wash precipitate.</td></tr>
<tr><td rowspan="2">Precipitate:
Group III
as sulfides, hydroxides).
See Table VI.</td><td colspan="2">(13) Filtrate: Add $(NH_4)_2CO_3$. Filter, wash precipitate.</td></tr>
<tr><td>Precipitate:
Group IV
(as carbonates).
See Tables IX, X.</td><td>Filtrate:
Group V.
See Table XI.</td></tr>
</table>

---

[1] The numbers in parentheses refer to the corresponding paragraphs in the detailed analytical procedure. Underscoring indicates precipitates.

GROUP I. THE HYDROCHLORIC ACID GROUP

This group contains the cations whose chlorides are insoluble both in water and in dilute HCl. The membership of the group is

Lead, Pb^{++}.
Silver, Ag^{+}.
Mercurous mercury, Hg_2^{++}.

Lead chloride is slightly soluble in cold water and readily soluble in hot water. The result is that Pb^{++} is not completely precipitated in this group but appears also in Group II. If Pb^{++} is present in the solution in small quantity only, it may not be found at all in Group I, but wholly in Group II.

Note.—Lead chloride is freely soluble in neutral and alkaline solutions containing acetates, tartrates, and a number of other anions. Upon acidification with HCl, however, the $PbCl_2$ will be precipitated more or less completely.

PRELIMINARY EXPERIMENTS

(15) Lead, Pb^{++}. (*a*) *Solubility of Lead Chloride.*—Place 1 or 2 drops of lead nitrate solution, $Pb(NO_3)_2$, in a test tube, dilute to about 1 ml., and add dilute HCl, drop by drop, with shaking, as long as the amount of precipitate appears to increase (E). Settle by standing or centrifuging and pour off the supernatant liquid. Wash the precipitate by adding a few drops of water, mixing, settling, and again decanting the supernatant layer. Now add 1 ml. of water and place the test tube in a beaker of boiling water. Save the solution for the next experiment.

Note.—Write the names and most important properties below the formulas of the new substances formed, *e.g.*,

$$Pb^{++} + 2Cl^{-} \rightarrow \underset{\substack{\text{Lead chloride,}\\ \text{white, soluble}\\ \text{in hot water}}}{PbCl_2}.$$

(*b*) *Lead Chromate.*—To a portion of the solution reserved from (**15**), add 1 or 2 drops of potassium dichromate solution, $K_2Cr_2O_7$. The yellow precipitate is lead chromate, $PbCrO_4$ (E). Divide the mixture into two parts and use one to test the solubility of the precipitate in $HC_2H_3O_2$ (?) and the other to test the solubility in dilute HNO_3 (E).

Other reactions of the Pb^{++} ion will be considered under Group II.

(16) Silver, Ag^+. (*a*) *Insolubility of Silver Chloride in Water.* Take 1 drop of silver nitrate solution, $AgNO_3$, dilute to about 1 ml., and add dilute HCl dropwise, with shaking, until precipitation is complete (?). Centrifuge (or shake well) and decant. Reserve precipitate for later experiments.

Try the solubility of AgCl in hot water by adding 1 ml. of water to the precipitate and heating in a water bath. Decant the clear solution, dilute it to about 50 ml., and test the solution for Ag^+ by saturating it with H_2S (?). (SEPARATION OF Ag^+ FROM Pb^{++}.) Is AgCl soluble in water? Save the residue for the next experiment.

(*b*) *The Silver-Ammonia Complex.*—Suspend the AgCl precipitate from the preceding experiment in 1 ml. of water and add NH_4OH dropwise, with shaking, until the precipitate is dissolved (?, E). The Ag^+ combines with the NH_3 of the NH_4OH to give $Ag(NH_3)_2^+$. Acidify this ammoniacal solution with dilute HNO_3 (?, E).

(*c*) *Silver Sulfide.*—Dilute 1 or 2 drops of $AgNO_3$ solution to about 5 ml. in a small Erlenmeyer flask and saturate with H_2S (Instructions). Write the equation and describe the precipitate. Transfer the mixture to a test tube, centrifuge, and wash. Test the solubility of the precipitate in dilute HCl (?). What will become of Ag^+ ions if they are not completely precipitated as AgCl in Group I?

(17) Mercurous Mercury, Hg_2^{++}. (*a*) *Mercurous Chloride.*—Dilute 1 or 2 drops of mercurous nitrate solution, $Hg_2(NO_3)_2$, to about 1 ml. and add dilute HCl dropwise, with stirring, until the precipitation of Hg_2Cl_2 is complete (E). Centrifuge or filter, and wash the precipitate with cold water. Test portions of the precipitate for its solubility in hot water, in dilute HCl, and in dilute aqua regia (E). Reserve the main part of the precipitate for the following experiment.

Note.—Solutions of mercurous salts usually contain mercuric salts, owing to the ready oxidation of the former by the oxygen of the air.

(*b*) *Reaction of Mercurous Chloride with Ammonia.*—Add NH_4OH to the precipitate reserved from the preceding experiment (?, E). The solid residue consists of $Hg + HgNH_2Cl$. (SEPARATION OF Hg_2^{++} FROM Ag^+.)

Exercises

1. Criticize the following definition of Group I: "Group I consists of the metals insoluble in dilute HCl."
2. Fill in the blanks in the following table by the words "soluble" or "insoluble."

	HOT WATER	NH_4OH
Lead chloride.................	....	....
Silver chloride................	....	....
Mercurous chloride............	....	....

3. What ion of Group I forms a chloride appreciably soluble in cold water?
4. Point out the possible errors in technique when $PbCl_2$ is present in the HCl precipitate and yet is not found by the $K_2Cr_2O_7$ test.
5. What would be the result if, in analyzing a solution containing $AgNO_3$ and $Ba(NO_3)_2$, the AgCl was not thoroughly washed? Remember that $BaCrO_4$ is yellow and insoluble in $HC_2H_3O_2$.
6. Name some reagents besides HNO_3 that might be used to precipitate AgCl from a solution containing $Ag(NH_3)_2Cl$.
7. What is a common impurity in mercurous salt solutions? Explain its source.
8. Criticize the following equation: $Hg_2Cl_2 + NH_4OH$ (excess) $\rightarrow HgNH_2Cl + Hg + HCl + H_2O$.
9. Dilute HCl is added to a hot solution of a Group I unknown without effect; a white precipitate, however, forms on cooling. What members of the group are indicated?
10. A solution gives with dilute HCl a white precipitate insoluble in hot water and insoluble in NH_4OH but blackened by the latter. Interpret.
11. How could you distinguish between $PbCl_2$, Hg_2Cl_2, and AgCl by the use of the single reagent NH_4OH?
12. What effect does vigorous shaking have on the physical form of an AgCl precipitate?
13. Arrange the chlorides of Ag^+, Hg_2^{++}, and Pb^{++} in the order of their solubility. In case of a shortage of Cl^-, which one would not be precipitated?

14. Which is the better for washing a $PbCl_2$ precipitate, cold water or cold dilute HCl?
15. What is the proper wash for a Group I precipitate? Explain.
16. Formulate the equilibrium existing in a solution of AgCl in NH_4OH. Explain the shift upon adding HNO_3 to the mixture.
17. $K_2Cr_2O_7$ is added to a Pb^{++} solution, giving a precipitate of $PbCrO_4$. Formulate the equilibriums present in the mixture. How would these equilibriums be affected by adding excess H^+ (*e.g.*, dilute HNO_3)?

ANALYSIS

(18) Precipitation.—If the solution contains Group I only, not more than 0.5 ml. should be used as a sample; if it is a "general unknown" and may possibly contain all the cation groups, use a 1-ml. portion. Dilute to 2 ml. and add dilute HCl dropwise, with stirring, until precipitation is complete. Settle by standing or centrifuging, and decant the solution. Wash the precipitate twice by decantation, using each time 1 ml. of water containing 1 drop of dilute HCl. Combine solution and washings and reserve for (**30**).

Note.—The purpose of the washing is to remove ions of later groups. The water removes Hg^{++}, etc., and HCl removes Bi^{+++} and Sb^{+++}, which tend to form insoluble basic salts.

(19) Lead.—To the residue in the original tube, add 1 ml. of water and place the tube in a beaker of boiling water. Stir the mixture with a glass fiber and pour off the hot solution. To the clear solution add 1 drop of $K_2Cr_2O_7$ solution and 1 drop of $HC_2H_3O_2$. A yellow precipitate of $PbCrO_4$ indicates the presence of *lead*.

If Pb^{++} is found, continue the washing with hot water until the washings no longer give a precipitate with $K_2Cr_2O_7$.

(20) Silver.—Add a few drops of NH_4OH to the precipitate in the test tube and mix well. After centrifuging, pour off the supernatant liquid and acidify it with a few drops of dilute HNO_3. A white precipitate of AgCl indicates the presence of *silver*.

(21) Mercurous Mercury.—If the residue in the tube is blackened by the NH_4OH, the presence of *mercurous mercury* is indicated.

TABLE II.—ANALYSIS OF GROUP I

<table>
<tr><td colspan="4">(18) Solution (neutral, or slightly acid), possibly containing subsequent groups. Dilute 0.5 ml. of a Group I unknown or 1 ml. of a general unknown to 2 ml.; add dilute HCl. Filter, wash precipitate with dilute HCl cold water.</td></tr>
<tr><td colspan="3">Precipitate: $PbCl_2$, $AgCl$, Hg_2Cl_2. (19) Extract the precipitate with hot water.</td><td rowspan="3">Filtrate: Groups II, III, IV, V. See Table III.</td></tr>
<tr><td rowspan="2">Solution: $PbCl_2$. Add $K_2Cr_2O_7$. Precipitate: Yellow $PbCrO_4$.</td><td colspan="2">Residue: $AgCl$, Hg_2Cl_2. (20) Extract with NH_4OH.</td></tr>
<tr><td>Filtrate: $Ag(NH_3)_2^+ + Cl^-$. Add dilute HNO_3. Precipitate: White $AgCl$.</td><td>(21) Residue: $HgNH_2Cl + Hg$ (black).</td></tr>
</table>

GROUP II. THE HYDROGEN SULFIDE GROUP

This group contains the cations whose chlorides are soluble, and whose sulfides are insoluble, in dilute HCl. The membership is as follows:

THE COPPER SUBGROUP	THE TIN SUBGROUP
Mercuric, Hg^{++}	Arsenious, As^{+++}
Lead, Pb^{++}	Arsenic, As^{+++++}
Bismuth, Bi^{+++}	Antimonious, Sb^{+++}
Cupric, Cu^{++}	Antimonic, Sb^{+++++}
Cadmium, Cd^{++}	Stannous, Sn^{++}
	Stannic, Sn^{++++}

The division into subgroups is based on the solubility of the sulfides in ammonium sulfide, $(NH_4)_2S_x$.

Note.—Some of the formulas in the above list are more ideal than actual. Pentavalent arsenic occurs almost wholly as AsO_4^{---} instead of As^{+++++}, and pentavalent antimony as SbO_4^{---}, and not Sb^{+++++}. In HCl solution, stannic tin appears to be present as $SnCl_6^{--}$ instead of Sn^{++++}.

PRELIMINARY EXPERIMENTS

(22) Mercuric Mercury, Hg^{++}. (*a*) *Mercuric Sulfide.*—Dilute 1 or 2 drops of mercuric chloride solution, $HgCl_2$, to 1 ml., add 1 drop of dilute HCl, and saturate the mixture with H_2S (E).

Note any changes in color that take place (?). Settle, wash the precipitate with a little water, and reserve it for further tests.

Shake the precipitate up with a little water and transfer a portion to a small test tube. After settling, drain off the water and try the solubility of the precipitate in hot dilute HNO_3 (1 drop of dilute HNO_3 + 2 drops of water), heating in a water bath. (SEPARATION OF HGS FROM PBS, BI_2S_3, CUS, CDS.) In the same way, drain the remainder of the precipitate and try its solubility in aqua regia (3 drops of dilute HCl + 1 drop of dilute HNO_3), heating as before in a water bath. What is the undissolved residue? Complete the equation: $HgS + HCl + HNO_3 \rightarrow ?$.

Notes.—1. The precipitate formed by H_2S with a solution of $HgCl_2$ shows the following succession of colors: white, yellow, brown, black. The final black substance is HgS. The others are mixed salts, intermediate in composition between $HgCl_2$ and HgS, *e.g.*, $HgCl_2.2HgS$ (white).

2. The insolubility of HgS in hot 2*M* HNO_3 is due to its extremely low solubility in water; *e.g.*, it is only the dissolved portion that reacts with the solvent acid. HgS is by far the most insoluble sulfide of the Copper Subgroup.

3. HgS slowly dissolves in dilute HNO_3 upon prolonged boiling, owing to the acid becoming more concentrated. The HgS is first changed into insoluble $Hg(NO_3)_2.2HgS$, and later into soluble $Hg(NO_3)_2$.

4. Aqua regia is made, as stated above, by mixing 3 volumes of HCl with 1 volume of HNO_3, and heating. Free chlorine is evolved, the equation being approximately: $3HCl + HNO_3 \rightarrow 3Cl + 2H_2O + NO$. The solvent action of aqua regia was formerly attributed to "nascent" chlorine, *i.e.*, a very active form of chlorine, just liberated from combination with hydrogen in HCl. It is more probable that the solvent effect is due to a combination of the oxidizing power of the HNO_3 and the complexing action of Cl^- ions with Hg^{++}, forming unionized $HgCl_2$ molecules.

(*b*) *Reduction of Mercuric Chloride by Stannous Chloride.*—Dilute 2 or 3 drops of $HgCl_2$ solution to about 1 ml. and add 1 drop of stannous chloride solution, $SnCl_2$, mixing promptly (?). Next dilute 2 or 3 drops of $SnCl_2$ to 1 ml. and add 1 drop of $HgCl_2$, mixing promptly (?). Note that the product of the reaction between $HgCl_2$ and $SnCl_2$ solutions depends on the relative amounts of these substances. Complete and balance:

$$HgCl_2 \text{ (excess)} + SnCl_2 \rightarrow ? + ?$$
$$HgCl_2 + SnCl_2 \text{ (excess)} \rightarrow ? + ?$$

(23) Lead, Pb^{++}. (*a*) *Lead Sulfide.*—Acidify about 0.5 ml. of lead chloride solution, $PbCl_2$, with 1 drop of dilute HCl and saturate with H_2S (?). Settle and wash the precipitate and try its solubility in hot, dilute HNO_3 (1 ml. of dilute HNO_3 + 2 ml. of water), heating in a water bath (E). (SEPARATION OF Pb^{++} FROM HgS.) What is the undissolved residue?

Notes.—1. The insoluble residue left when HNO_3 reacts with a sulfide is sulfur. It is frequently discolored by the inclusion of small amounts of undissolved sulfide.

2. H_2S is not given off when HNO_3 reacts with sulfides. H_2S is an active reducing agent and reduces HNO_3 thus: $3H_2S + 2HNO_3 \rightarrow 4H_2O + 2NO + 3S$.

(*b*) *Conversion of Lead Nitrate into Lead Sulfate.*—To 1 or 2 drops of lead nitrate solution, $Pb(NO_3)_2$, in a small casserole, add 1 or 2 drops of dilute H_2SO_4 and mix well. Evaporate to dryness but do not bake. Complete the equation: $Pb^{++} + NO_3^- + H^+ + SO_4^{--} + \text{heat} \rightarrow ? + ? + ?$.

After the casserole has cooled, carefully wash the precipitate into a test tube with a little cold water. (SEPARATION OF Pb^{++} FROM Bi^{+++}, Cu^{++}, Cd^{++}.) (*Caution:* Never add water to hot H_2SO_4. Why?) Reserve the precipitate for further tests.

Note.—The evaporation with H_2SO_4 is necessary to expel nitrates, which increase the solubility of $PbSO_4$ considerably. Expressing the equilibrium by molecular formulas, we have $Pb(NO_3)_2 + H_2SO_4 \rightleftarrows PbSO_4 + 2HNO_3$. Of these four substances, HNO_3 has the lowest boiling point and consequently is the first to be evaporated. Its loss shifts the equilibrium to the right of the equation as here written, converting the Pb^{++} completely into $PbSO_4$.

(*c*) *Solubility of Lead Sulfate.*—Suspend in water the precipitate reserved from the preceding experiment and divide the suspension into two parts. Using the first portion, test the solubility of $PbSO_4$ in a few drops of NaOH solution (?). Complete the following equation:

$$PbSO_4 + OH^- \text{ (excess)} \rightarrow$$

To what class of hydroxides does $Pb(OH)_2$ belong? Acidify the alkaline solution with a few drops of acetic acid, $HC_2H_3O_2$ (E), and add 1 drop of $K_2Cr_2O_7$ solution (?). Complete the equation:

$$Pb(C_2H_3O_2)_2 + Cr_2O_7^{--} + H_2O \rightarrow$$

Test the solubility of the remaining portion of the $PbSO_4$ suspension in ammonium acetate solution, $NH_4C_2H_3O_2$ (E). What would happen if 1 drop of $K_2Cr_2O_7$ was added to the mixture? Try it.

Note.—The solvent action of acetate solutions on $PbSO_4$ is usually explained as due to the stability (*i.e.*, the low ionization) of $Pb(C_2H_3O_2)_2$ molecules. According to this theory, $PbSO_4$, although only slightly soluble, supports a higher concentration of Pb^{++} in the solution than the soluble $Pb(C_2H_3O_2)_2$. The equilibrium may be formulated thus:

$$\left.\begin{array}{l} 2NH_4C_2H_3O_2 \rightleftarrows 2NH_4^+ + 2C_2H_3O_2^- \\ \underline{PbSO_4} \rightleftarrows PbSO_4 \rightleftarrows SO_4^{--} + Pb^{++} \end{array}\right\} \rightleftarrows Pb(C_2H_3O_2)_2$$

(24) Bismuth, Bi^{+++}. (*a*) *Hydrolysis of Bismuth Salts.*—Add water dropwise to 2 or 3 drops of bismuth trichloride solution, $BiCl_3$, until a turbidity appears. Redissolve the precipitate by adding concentrated HCl dropwise. Express both reactions by a single equation (E). What names are given to this precipitate?

Suspensions of these basic salts give all the reactions of the Bi^{+++} ions.

Note.—The hydrolysis of bismuth salts involves the following fundamental reaction: $Bi^{+++} + H_2O \rightleftarrows BiO^+ + 2H^+$. Note that the reaction is reversible, so that both ions, Bi^{+++} and BiO^+, are present in all solutions.

(*b*) *Bismuth Sulfide.*—Dilute 2 drops of bismuth nitrate solution, $Bi(NO_3)_3$, to about 3 ml. This may cause a precipitate of white bismuthyl nitrate, $BiONO_3$. Saturate the mixture with H_2S (?, E). Centrifuge (or filter), wash the precipitate, and test its solubility in hot dilute HNO_3 (2 drops of dilute HNO_3 + 4 drops of water), heated in a hot-water bath. (SEPARATION OF Bi^{+++} FROM HgS.)

(*c*) *Bismuthyl Sulfate.*—What would happen if $Bi(NO_3)_3$ were "fumed down" with H_2SO_4 (E), and the product diluted with water (E)?

(*d*) *Bismuth Hydroxide.*—To 1 or 2 drops of $BiCl_3$ in a test tube add NaOH, at first drop by drop (?, E), and then in excess (*i.e.*, 1 ml.). Does $Bi(OH)_3$ appear to be amphoteric?

Repeat the experiment, using NH_4OH instead of NaOH (?, E). Does Bi^{+++} form soluble complexes with NH_3? (SEPARATION OF Bi^{+++} FROM Cu^{++} AND Cd^{++}.) Reserve one of the precipitates.

(*e*) *Reduction of Bismuth Hydroxide by Stannites.*—Wash one of the $Bi(OH)_3$ precipitates from the preceding experiment, best by centrifugation and decantation.

Prepare some sodium stannite solution, $NaHSnO_2$, as follows: Dilute 1 or 2 drops of $SnCl_2$ with 2 ml. of water and add NaOH, mixing well after each drop. A permanent precipitate will form, which later dissolves in the excess NaOH. Complete the following equations:

$$Sn^{++} \text{ (excess)} + OH^- \rightarrow$$
$$Sn(OH)_2 + OH^- \text{ (excess)} \rightarrow$$

Now add the $NaHSnO_2$ solution to the $Bi(OH)_3$ precipitate (?). Balance the equation: $Bi(OH)_3 + HSnO_2^- \rightarrow Bi + HSnO_3^- + H_2O$.

Note.—$NaHSnO_2$ solutions are not stable and must be made up as needed. They tend to decompose, especially upon heating, into tin (black) and $NaHSnO_3$: $HSnO_2^-$ (red. agt.) + $HSnO_2^-$ (ox. agt.) $\rightarrow Sn + HSnO_3^- + OH^-$.

(25) **Copper, Cu^{++}.** (*a*) *Cupric Sulfide.*—Dilute 1 or 2 drops of cupric nitrate solution, $Cu(NO_3)_2$, to about 2 ml. and saturate with H_2S. Centrifuge, wash, and divide the precipitate into two portions. Try the solubility of one portion in hot 2*M* HNO_3 (1 drop dilute HNO_3 + 2 drops water) (?, E). (SEPARATION OF Cu^{++} FROM HgS.) Try the solubility of the second portion in hot dilute H_2SO_4 (?). (SEPARATION OF CuS FROM Cd^{++}.)

(*b*) *Conversion of Cupric Nitrate into Cupric Sulfate.*—Write the equation for the reaction, when $Cu(NO_3)_2$ is "fumed down" with H_2SO_4 (E). Is the boiling necessary for this reaction? If so, it should be indicated in the equation.

(*c*) *Cupric-Ammonia Complex Ion.*—Dilute 1 or 2 drops of $Cu(NO_3)_2$ solution to 2 ml. and add NH_4OH drop by drop. A precipitate of $Cu(OH)_2$ may appear but will dissolve in excess NH_4OH. (SEPARATION OF Cu^{++} FROM $Bi(OH)_3$.) Complete the equation: $Cu^{++} + NH_4OH \rightarrow Cu(NH_3)_4^{++} + H_2O$. Note the color of the complex ion (?). Reserve the solution for the following experiment.

(*d*) *The Cuprocyanide Complex Ion.*—To the blue solution reserved from the preceding experiment, add sodium cyanide solution, NaCN, drop by drop, until the color is completely removed. The solution now contains a complex copper cyanide anion, whose formula is usually written $Cu(CN)_2^-$. Complete and balance:

$$Cu(NH_3)_4^{++} + CN^- \rightarrow \underline{Cu(CN)_2} \text{ (yellow-green)} + ?$$
$$\underline{Cu(CN)_2} \rightarrow \underline{Cu_2(CN)_2} \text{ (white)} + C_2N_2 \text{ (cyanogen)}$$
$$\underline{Cu_2(CN)_2} + CN^- \text{ (excess)} \rightarrow Cu(CN)_2^-$$

Saturate this solution with H_2S (?). No precipitate forms, showing that the complex ion is very stable; *i.e.*, it gives too few cuprous ions, Cu_2^{++}, to react with H_2S.

(*e*) *Cupric Ferrocyanide.*—Dilute 1 drop of $Cu(NO_3)_2$ solution until the blue color of the Cu^{++} ion is no longer visible. Acidify with 1 drop of dilute H_2SO_4 and add 1 drop of potassium ferrocyanide solution, $K_4Fe(CN)_6$ (E).

(*f*) *Displacement of Copper by Iron.*—Dilute 1 or 2 drops of $CuSO_4$ solution to 2 ml. and introduce a small amount of iron—*e.g.*, a small nail or brad. Heat the tube in a water bath until the blue color of the Cu^{++} ion has completely disappeared (E). Decant the solution, add 1 or 2 drops of dilute HCl, and saturate with H_2S (?). (SEPARATION OF Cu^{++} FROM Cd^{++}.) Name two other metals that would displace Cu^{++} in a similar way (?). (See Appendix, page 140.)

(26) Cadmium, Cd^{++}. (*a*) *Cadmium Sulfide.*—Dilute 1 or 2 drops of cadmium nitrate solution, $Cd(NO_3)_2$, and saturate with H_2S (?, E). Wash and divide the precipitate into two portions. Try the solubility of one portion in hot $2M$ HNO_3 (1 drop of dilute HNO_3 + 2 drops of water) (?, E). (SEPARATION OF Cd^{++} FROM HgS.) Try the solubility of the second portion in hot dilute H_2SO_4 (?, E). (SEPARATION OF Cd^{++} FROM CuS.)

Note.—The color and composition of the precipitate vary somewhat with the conditions. From hot, acidified $CdCl_2$, orange $CdCl_2.CdS$ is thrown down; from cold, neutral $CdCl_2$, yellow CdS is the main product.

(*b*) *The Cadmium-Ammonia Complex Ion.*—Dilute 1 or 2 drops of $Cd(NO_3)_2$ solution to 2 ml. and add NH_4OH dropwise. A white precipitate of $Cd(OH)_2$ may appear but will dissolve in excess NH_4OH. [SEPARATION OF Cd^{++} FROM $Bi(OH)_3$.] Write equation. Reserve the solution for the following experiment.

(*c*) *Cadmium Ferrocyanide.*—Dilute 1 or 2 drops of $Cd(NO_3)_2$ to about 2 ml. and add 1 drop of $K_4Fe(CN)_6$ solution (?, E).

Now add 1 drop of $Cu(NO_3)_2$ solution and mix well. Which is the more insoluble, $Cu_2Fe(CN)_6$ or $Cd_2Fe(CN)_6$? How would you test for Cu^{++} in the presence of Cd^{++}?

(*d*) *Displacement.*—Would Cd^{++} be displaced from solution by iron, as in the case of Cu^{++}? (See Electromotive Series, page 140.)

(*e*) *The Cadmium-Cyanide Complex Ion.*—Add 2 drops of NaCN solution to the solution reserved from the preceding experiment. Complete the equations:

$$Cd(NH_3)_4^{++} + CN^- \rightarrow \underline{Cd(CN)_2} \text{ (white)} + ?$$
$$\underline{Cd(CN)_2} + CN^- \text{ (excess)} \rightarrow Cd(CN)_4^{--}$$

Saturate the solution with H_2S (?, E). Which gives the higher Cd^{++} concentration, $Cd(CN)_4^{--}$ or CdS? Compare results with $Cu(CN)_2^-$(**25,** *d*) above. (SEPARATION OF CDS FROM Cu^{++}.)

(27) Arsenic, As^{+++} and AsO_4^{---}. (*a*) *The Sulfides.*—Dilute 1 or 2 drops of arsenic trichloride solution, $AsCl_3$, to about 2 ml. and saturate with H_2S (?, E). Note that the precipitate forms immediately. Reserve the precipitate for (*b*), below.

Note.—$AsCl_3$ solution is prepared by dissolving As_2O_3 in excess HCl and therefore contains free HCl.

Dilute 1 or 2 drops of arsenic acid solution, H_3AsO_4, to 2 ml. and saturate with H_2S (?). Heat the mixture and resaturate with H_2S. Does heating improve the speed of precipitation?

Next, dilute 1 or 2 drops of H_3AsO_4 with 2 ml. of concentrated HCl and saturate with H_2S (?). What effect does high acidity have on the rate of precipitation?

Finally, dilute 1 or 2 drops of H_3AsO_4 with 2 ml. of dilute HCl and add 1 drop of NH_4I solution. Saturate with H_2S (?). How does the presence of I^- ions affect the rate of precipitation?

Reserve these precipitates for the following experiments.

Note.—The action of I^- in hastening the precipitation of arsenic sulfide from arsenates depends on the fact that HI (formed by the action of HCl on NH_4I) rapidly reduces H_3AsO_4 to H_3AsO_3, which reacts rapidly with H_2S, while H_3AsO_4 reacts slowly. The HI is continuously regenerated by the H_2S from the I_2 formed in the reduction of the H_3AsO_4. The equations involved are:

(1) $2H_3AsO_4 + 4HI \rightarrow 2H_3AsO_3 + 2H_2O + 2I_2$
(2) $2H_3AsO_3 + 3H_2S \rightarrow As_2S_3 + 6H_2O$
(3) $2I_2 + 2H_2S \rightarrow 4HI + 2S$

Adding and canceling substances occurring on both sides, the total equation is

$$2H_3AsO_4 + 5H_2S \rightarrow As_2S_3 + 2S + 8H_2O$$

(*b*) *Ammonium Thioarsenate.*—Wash a little of the As_2S_3 precipitate from (**27**, *a*), add 2 ml. of $(NH_4)_2S_x$, and heat for a few moments in the hot-water bath. (SEPARATION FROM THE COPPER SUBGROUP.) The final solution contains ammonium thioarsenate, $(NH_4)_3AsS_4$: $As_2S_3 + 3S^{--} + 2S \rightarrow 2AsS_4^{---}$. Save the solution.

Repeat the experiment, using the As_2S_5 precipitated from H_3AsO_4. Complete the equation: $As_2S_5 + S^{--} \rightarrow$? Note the identity of the product with that in the preceding test.

Acidify a little of the $(NH_4)_3AsS_4$ solution with dilute HCl (?). Balance the equation: $AsS_4^{---} + H^+ \rightarrow As_2S_5 + H_2S$. Reserve the precipitate for the following experiment.

Note.—In writing equations, consider $(NH_4)_2S_x$ as consisting of $(NH_4)_2S + S$.

(*c*) *Solution of As_2S_5 in HNO_3.*—To a little of the As_2S_5 reserved from the preceding experiment, add 2 ml. of dilute HNO_3 and heat the mixture in the water bath for several minutes (?). What is the floating residue? Complete and balance the equations:

$$As_2S_5 + HNO_3 + H_2O \rightarrow H_3AsO_4 + S + NO$$
$$S + HNO_3 \rightarrow H_2SO_4 + NO \text{ (slow, incomplete)}$$

(*d*) *Silver Arsenate.*—Place a drop of H_3AsO_4 in a test tube and add a drop of $AgNO_3$ (?). Next add 1 ml. of 10 per cent $NH_4C_2H_3O_2$. Complete the equations:

$$H_3AsO_4 + Ag^+ \rightarrow Ag_3AsO_4 + H^+$$
$$H^+ + C_2H_3O_2^- \rightarrow HC_2H_3O_2 \text{ (a weak acid)}$$

Is Ag_3AsO_4 soluble in HNO_3 (?), in $HC_2H_3O_2$ (?).

(**28**) **Antimony, Sb^{+++}.** (*a*) *Hydrolysis of Antimony Salts.*—Add 1 or 2 drops of antimony trichloride solution, $SbCl_3$, to 2 ml. of water (?). Now add concentrated HCl, drop by drop, mixing well after each addition (?). Write a single reversible equation to represent both reactions (E). What is the name of the SbO^+ ion? The salts of what other metal have been found to hydrolyze similarly?

(*b*) *Antimony Sulfide.*—Dilute 1 or 2 drops of $SbCl_3$ solution to about 5 ml. in an Erlenmeyer flask. Pay no attention to any precipitate of SbOCl. Saturate the mixture with H_2S (?, E). Transfer a portion of the precipitate to a test tube, wash it, and try its solubility in warm $(NH_4)_2S_x$ (?, E). What is the name of the product? Write the equation for acidifying the SbS_4^{---} ion with H^+ (E).

Test the solubility of another portion of Sb_2S_3 in hot concentrated HCl (?, E).

(*c*) *Displacement of Metallic Antimony.*—Place a small piece of Al wire in a test tube containing 1 or 2 drops of $SbCl_3$ solution and warm in water bath for several minutes (E). (SEPARATION OF SB FROM SN^{++}.) What is the color of the precipitate? Refer to the e.m.f. table and list several other metals that will displace Sb from its ionic form.

(29) Stannous Tin, Sn^{++}; Stannic Tin, Sn^{++++}. (*a*) *Sulfides.* Dilute 2 drops of stannous chloride solution, $SnCl_2$, to about 3 ml. and saturate with H_2S (?, E). Treat a sample of stannic chloride solution, $SnCl_4$, in a similar way (E). Record the colors of these sulfides and reserve them for later tests.

Note.—$SnCl_2$ and $SnCl_4$ solutions always contain considerable amounts of free HCl to prevent hydrolysis. The precipitation of the tin sulfides therefore takes place in acid solution, as is the case with other members of Group II.

Transfer a portion of the SnS_2 precipitate to a test tube, centrifuge, and drain off the liquid. Add concentrated HCl to the precipitate and heat in a hot-water bath (?, E). (SEPARATION OF SN FROM AS.)

(*b*) *Ammonium Thiostannate.*—Suspend portions of the SnS and SnS_2 precipitates in NH_4OH and saturate with H_2S (?, E). Which one is insoluble in colorless ammonium sulfide, $(NH_4)_2S$? To the unchanged mixture add a few drops of yellow ammonium polysulfide, $(NH_4)_2S_x$, and warm gently in a water bath. Acidify the resultant solution with dilute HCl. (SEPARATION OF SN FROM COPPER SUBGROUP.) Complete and balance the equations:

$$SnS_2 + S^{--} \rightarrow$$
$$SnS + S^{--} + S \rightarrow$$
$$SnS_3^{--} + H^+ \rightarrow$$

(*c*) *Reduction of* Sn^{++++} *by Metals.*—Warm separate portions of dilute $SnCl_4$ solution in the hot-water bath with small pieces of Al (wire), Pb (sheet), Zn (mossy), and Fe (nail). If any of these metals should dissolve completely, more may be added. Examine the residues and identify the reduction products. If the surface of the metal remains clean, look for the reduction product in the solution. (SEPARATION OF SN FROM SB.) Write balanced equations.

Note.—Saturation of NH_4OH with H_2S gives colorless ammonium sulfide, thus: $2NH_4OH + H_2S \rightarrow (NH_4)_2S + H_2O$. Upon warming colorless $(NH_4)_2S$ with sulfur, yellow ammonium sulfide (also called "ammonium polysulfide") is formed, thus: $(NH_4)_2S + (x - 1)S \rightarrow (NH_4)_2S_x$.

(*d*) *Reducing Action of Stannous Chloride.*—Recall the reactions between $HgCl_2$ and $SnCl_2$ (two stages) from (**22**, *b*). Write equations.

(*e*) *Metastannic Acid.*—Place a piece of metallic tin not larger than a grain of rice in a test tube and add about 1 ml. of concentrated HNO_3. Warm as long as there is any apparent reaction (?, E). Wash the precipitate several times by centrifugation and decantation, to remove nitrates. Then add 1 ml. of concentrated HCl, 1 ml. of water, and a small piece of Al (wire) or Zn (mossy) and warm in the hot-water bath for 2 or 3 min. Dilute and cool the solution and add 1 drop of $HgCl_2$ solution.

This procedure is very useful in testing insoluble precipitates for Sn. (See page 36.)

Exercises

1. $Bi(NO_3)_3$ solution may give a precipitate of BiOCl with dilute HCl. Why, then, is Bi^{+++} not in Group I? Recall definition of Group I.
2. What are the names of the subgroups of Group II? What is the basis of this grouping?
3. Explain the recurrence of Pb^{++} in Group II. Does the same explanation hold for Hg^{++}?
4. What step in Group II might be omitted if Pb^{++} were known to be absent?
5. What is the gas evolved when a sulfide dissolves in dilute HNO_3? Explain why it cannot be H_2S.

6. Could $PbSO_4$ be converted into $Pb(NO_3)_2$ by evaporating it with an excess of concentrated HNO_3?

7. Calculate the concentration of the acid if 4 ml. of dilute HCl ($6M$) is diluted to a volume of 100 ml.

8. Give names and formulas of the products obtained when the following are dissolved in (*a*) $(NH_4)_2S$ and (*b*) $(NH_4)_2S_x$: As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5.

9. What is the meaning of the prefix "thio"?

10. What is the effect of the presence of NH_4^+ salts on the ionization of NH_4OH?

11. What kind of agent is the excess sulfur in $(NH_4)_2S_x$? Illustrate by its reaction with As_2S_3 or SnS.

12. What is the color of the sulfur precipitated from $(NH_4)_2S_x$ upon precipitation with an acid (*a*) before boiling? (*b*) After continued boiling?

13. What substance is used to catalyze the precipitation of arsenic sulfide from arsenate solutions by means of H_2S?

14. Refer to the Electromotive Series in the Appendix (page 140) and explain why Fe is the most suitable metal for separating Cu^{++} from Cd^{++}. What would happen if Zn was used?

15. What are the two stages in the reduction of Sn^{++++}? The use of lead gives which product mainly?

16. AgCl is less soluble than Ag_3AsO_4. What would happen if a precipitate of Ag_3AsO_4 was washed with a solution containing NH_4Cl? Would Ag_3AsO_4 ever form in the presence of an excess of chlorides?

17. Why will oxalate solutions dissolve $Sb(OH)_3$ and not Sb_2S_3?

18. Indicate reagents and principal products in the following one-step separations:

(*a*) $\left\{\begin{matrix} Bi^{+++} \\ Cd^{++} \end{matrix}\right\}$ ····(reagent)················→ .... (products)

(*b*) $\left\{\begin{matrix} HgS \\ As_2S_5 \end{matrix}\right\}$ ··→ ....

(*c*) $\left\{\begin{matrix} Pb^{++} \\ Cu^{++} \end{matrix}\right\}$ ··→ ....

(*d*) $\left\{\begin{matrix} As_2S_5 \\ SnS_2 \end{matrix}\right\}$ ··→ ....

(*e*) $\left\{\begin{matrix} HgS \\ CdS \end{matrix}\right\}$ ··→ ....

19. Identify the following ions of Group II:

(*a*) What ion forms an insoluble sulfate?
(*b*) What ions form brown sulfides? yellow sulfides?
(*c*) What ion forms a yellow chromate soluble in NaOH solution?
(*d*) What ion forms a yellow sulfide soluble in $(NH_4)_2S_x$ and insoluble in concentrated HCl?
(*e*) What ions form NH_3 complexes?

(*f*) What ion of the Tin subgroup forms a sulfide insoluble in colorless $(NH_4)_2S$?

20. An unknown solution containing only Group II ions gives with H_2S a brown precipitate, partially soluble in $(NH_4)_2S_x$. The brown residue dissolves in dilute HNO_3 to a colorless solution which gives no precipitate with H_2SO_4 but a white one with NH_4OH. The yellow $(NH_4)_2S_x$ filtrate gives upon acidification a yellow precipitate, soluble in concentrated HCl. What ions are indicated?

21. Group II is precipitated in what concentration of HCl? What would result if the concentration were too high? too low?

22. What is the significance of the formation of a slight white precipitate when an acid solution is saturated with H_2S?

ANALYSIS

Owing to the complexity of this group, analysis on a semimicro scale is not practicable. Using only 1 or 2 drops as a sample, the inevitable losses in the various separations involved might reduce the amount of certain of the ions beyond the range of sensitiveness of their tests. In general, for complex solutions, 1-ml. samples should be used, and the volumes of the resultant solutions are proportionately larger.

Sometimes Group II unknowns contain precipitates. Such mixtures should be thoroughly shaken, so as to get a representative mixture. The precipitates usually contain such substances as the following: $PbCl_2$, white crystals, soluble in hot water; BiOCl and SbOCl, heavy white precipitates, soluble in dilute HCl; and $SnO_2.xH_2O$ ("metastannic acid"), white gelatinous precipitate, insoluble in hot HCl.

Notes.—1. With the exception of $SnO_2.xH_2O$, these precipitates do not interfere with the usual course of an analysis. H_2S converts them into sulfides almost as readily as if they were in solution. $SnO_2.xH_2O$, on the other hand, is slow in changing into SnS_2, and there is danger that Sn will be lost in the separation of the subgroups in (**33**). Hence, it is desirable to make a "side test" for Sn on any residue insoluble in the HNO_3 treatment in (**30**).

2. It should be noted that Sn may be present in Group II solutions containing no precipitate. The absence of a precipitate is therefore no indication of the absence of Sn.

Group II is separated from Groups III to V by means of H_2S in solutions of a definite acidity, *viz.*, 0.25 to 0.30 molar H^+.

Note.—In the case of neutral unknowns, it might appear that the proper acidity could be otained by using a definite amount of HCl in precipitating

Group I, and then diluting the solution to a definite volume. Usually this is true. However, in the presence of certain anions (*e.g.*, $C_2H_3O_2^-$), a buffer effect that prevents the realization of the proper acidity is produced.

(30) Regulation of Acidity.—Add 1 ml. of concentrated HNO_3 to the filtrate from Group I (or to 1 ml. of an unknown in Group II) and evaporate almost to dryness in a casserole. Be careful not to bake the residue. Add exactly 5 ml. of *M* HCl (side shelf) and warm gently. Transfer the solution to a 50-ml. Erlenmeyer flask. If an insoluble residue remains, wash it with 5 ml. of warm water, in small portions, and add the washings to the main solution. Reserve the residue for (**32**).

Notes.—1. Excess of acid must be removed, since a higher concentration of acid than 0.3 molar will prevent the complete precipitation of the more soluble sulfides, particularly PbS, CdS, and SnS.

2. Evaporation with concentrated HNO_3 removes the anions of all other acids (except the non-volatile acids like H_2SO_4 and H_3PO_4). $HgCl_2$ and $AsCl_3$, which are volatile in steam, are converted into non-volatile $Hg(NO_3)_2$ and H_3AsO_4. Organic matter, which may interfere with the precipitation of $Al(OH)_3$ and $Cr(OH)_3$ in Group III, is destroyed.

3. The removal of $C_2H_3O_2^-$ ions is of particular importance, since they exert a "buffer" action, reducing the effective concentration of the acid. To illustrate, Zn^{++} (a member of Group III) can be precipitated as ZnS from a solution containing the 5 cc. of dilute HCl prescribed above in the presence of moderate concentrations of $C_2H_3O_2^-$.

(31) Precipitation.—Place the flask containing the HCl solution from (**30**) in a beaker of hot water, add 1 drop of NH_4I solution, and saturate with H_2S (see page 8) for 5 min. If a yellow precipitate (As_2S_5) forms slowly, 15 or 20 min. may be necessary for complete precipitation. When precipitation is complete, add 15 ml. of cold water and resaturate this solution with H_2S in the cold for several minutes. Filter with gentle suction, wash, and reserve the precipitate for (**33**) and the filtrate for (**55**).

Notes.—1. Sometimes, upon adding the 15 cc. of cold water, a precipitate of BiOCl or SbOCl forms. Such precipitates cause no trouble, since they are readily converted into sulfides by H_2S.

H_2S sometimes produces a pure-white precipitate. This is finely divided sulfur, produced by the oxidation of the H_2S by oxidizing agents present in the solution. The most important of these are: Ferric salts (yellow-brown), which are reduced to ferrous salts (green); permanganates (purple), reduced to manganous salts (colorless); and chlorates and peroxides, which show no color change upon reduction. These color changes should be carefully noted, since they indicate the presence of certain substances in the solution.

3. The sulfides do not precipitate simultaneously but more or less in the order of their solubility, *viz.*, As_2S_3, HgS, CuS, Sb_2S_3, Bi_2S_3, SnS_2, PbS, SnS, and CdS. That is to say, little or none of any of these substances is precipitated until the precipitation of all the sulfides preceding it in the list is complete. As_2S_5, on account of its slow speed of formation, may be the last to form, notwithstanding the fact that it is the most insoluble sulfide of the group.

4. Many precipitated sulfides are colloidal substances, which clog up the pores of the filter paper; consequently the filtration proceeds very slowly. Heat and the presence of strong electrolytes (NH_4NO_3 and NH_4Cl are ordinarily used) make them more readily filterable. As far as possible, colloidal precipitates should be washed by decantation.

(32) Analysis of Insoluble Residue.—The residue reserved from (**30**) presumably consists of SnO_2 or Sb_2O_4 or both. Transfer it to a test tube, add a piece of zinc about the size of a grain of rice, and then add dilute HCl in small amounts, until the original zinc is dissolved. A black precipitate is probably metallic Sb. Filter the solution into a little $HgCl_2$ solution. A satin-white or gray precipitate indicates *tin*.

Dissolve the black residue by pouring through the paper a warm mixture of 2 ml. of dilute HNO_3 + 4 ml. of H_2O + 2 or 3 drops of tartaric acid, $H_2C_4H_4O_6$. Dilute the filtrate with an equal volume of water and saturate with H_2S. An orange precipitate of Sb_2S_3 indicates *antimony*.

Notes.—1. The zinc reduces the Sn^{++++} (from SnO_2) to Sn^{++} and the Sb^{+++} (from Sb_2O_4) to metallic Sb.

2. The detection of antimony at this point is infrequent, for Sb_2O_4 usually dissolves in warm *M* HCl.

(33) Separation into Subgroups.—By means of a fine stream of water from a wash bottle, transfer the precipitate from (**31**) to a 125-ml. Erlenmeyer flask. Add 2 ml. of NH_4OH and 2 drops of 3 per cent H_2O_2 solution and saturate the mixture with H_2S for at least 5 min. Shake occasionally to break down any lumps of the precipitate. Warm the mixture, filter, and wash. Reserve the residue for (**34**) and the filtrate for (**39**).

Notes.—1. In case the Group II precipitate is small and cannot be washed from the paper, both paper and precipitate may be transferred to the

Erlenmeyer flask and subjected to the NH_4OH-H_2S extraction. The paper may later be "fished out" of the solution and washed with a fine stream of water.

2. The NH_4OH and H_2S combine to form colorless ammonium sulfide, $(NH_4)_2S$.

3. The H_2O_2 is added to insure the oxidation of Sb^{+++} to Sb^{+++++}, and Sn^{++} to Sn^{++++}. The sulfides of the higher valences are soluble in $(NH_4)_2S$, while the sulfides of the lower valences are insoluble.

4. Care must be taken to use an excess of H_2S, in order to prevent CuS from passing into the Tin subgroup as a brown suspension.

TABLE III.—PRECIPITATION OF GROUP II AND SEPARATION OF THE COPPER AND TIN SUBGROUPS

<table>
<tr><td colspan="4">(30) Filtrate from Group I or unknown on Group II only. Add 1 ml. of conc. HNO_3, evaporate to a paste. Add 5 ml. <i>M</i> HCl (side shelf), warm gently, wash with 5 ml. warm H_2O. Filter.</td></tr>
<tr><td rowspan="3">(32) Residue: SnO_2, Sb_2O_4.
Add Zn + HCl.
Precipitate: Sb (black).
Solution: $SnCl_2$.
Add $HgCl_2$.
Precipitate: Hg_2Cl_2 (white). Hg (black).</td><td colspan="3">(31) Solution: Add 1 drop of NH_4I, saturate hot solution with H_2S. Dilute to 30 ml. and saturate cold mixture with H_2S. Filter, wash precipitate.
Arnold</td></tr>
<tr><td colspan="2">(33) Precipitate: HgS, PbS, Bi_2S_3, CuS, CdS, SnS_2, As_2S_3, Sb_2S_3, S.
Add 2 ml. NH_4OH and 3 drops of H_2O_2; saturate mixture with H_2S. Filter, wash precipitate.</td><td rowspan="2">Filtrate: Groups III, IV, V. See Table VI.</td></tr>
<tr><td>Residue: HgS, PbS, Bi_2S_3, CuS, CdS. See Table IV.</td><td>Filtrate: SnS_3^{--}, AsS_4^{---}, SbS_4^{---}, S^{--}. See Table V, VI</td></tr>
</table>

(**34**) **Mercury.**—Transfer the residue from (**33**) to a small beaker or casserole (along with the filter paper, if necessary) and drain off any solution. Add 4 ml. of water and 2 ml. of dilute HNO_3, and heat to incipient boiling for 1 min. or so, until the reaction is complete. Centrifuge and decant (or filter) and wash the residue. Combine washings with the main solution and reserve for (**35**).

Note.—The basis of the separation of HgS from the other sulfides of the Copper subgroup is its low solubility in water. That is, it does not give a high enough concentration of dissolved HgS to react with $2M$ HNO_3. The other sulfides are more soluble in water and for that reason react more readily with 2*M* HNO_3.

If the residue is yellowish or gray and tends to float in the hot HNO_3, it is probably only impure sulfur and may be discarded. If the residue is dark, Hg may be present. Heat the residue with about 2 ml. of dilute aqua regia (3 volumes of dilute HCl + 1 volume of dilute HNO_3) and filter out any insoluble residue (sulfur). To the filtrate add 2 or 3 drops of $SnCl_2$ solution. A satin-white precipitate of Hg_2Cl_2-Hg indicates the presence of *mercury*.

Notes.—1. Frequently the sulfur residue contains traces of PbS and CuS sufficient to give it a black color. Hence a black residue does not necessarily indicate Hg^{++}.

2. Dilute aqua regia is not so strong an oxidizing agent as concentrated aqua regia and does not perceptibly interfere with the action of $SnCl_2$ solution.

3. An excess of $SnCl_2$ is indicated, since any free Cl_2 must be reduced to Cl^- before the $HgCl_2$ will begin to be reduced.

(35) Lead.—To the filtrate from **(34)**, add 2 or 3 drops of dilute H_2SO_4 and evaporate almost to dryness in a small casserole. If heavy white fumes of H_2SO_4 are not evolved in the later stages of the evaporation, cool the casserole and add more dilute H_2SO_4. Repeat the evaporation. Cool the casserole and wash the residue into a test tube. A white precipitate is $PbSO_4$ or $(BiO)_2SO_4$. Centrifuge or filter, decant, and wash with a little very dilute H_2SO_4. Reserve the solution for **(36)**. Add a little water to the residue in the test tube and then 4 or 5 drops of NaOH solution. If there is no apparent action, decant the solution from the residue. Acidify the solution with $HC_2H_3O_2$ (litmus test) and add 1 drop of $K_2Cr_2O_7$ solution. An orange-yellow precipitate indicates the presence of lead.

The residue insoluble in NaOH is $(BiO)_2SO_4$ and indicates the presence of *bismuth.*

Notes.—1. The purpose of the evaporation with H_2SO_4 is the expulsion of NO_3^- as HNO_3. NO_3^- ions have a surprisingly large solvent action on $PbSO_4$.

2. $PbSO_4$ is somewhat soluble in concentrated H_2SO_4. Consequently the precipitate does not appear until the solution is diluted. Concentrated H_2SO_4 converts $PbSO_4$ into $Pb(HSO_4)_2$ according to the equation: $PbSO_4 + H_2SO_4 \rightleftarrows Pb(HSO_4)_2 + H_2O$. The double arrow indicates that the reaction tends to reverse upon the addition of water.

3. An excess of H_2SO_4 favors precipitating $PbSO_4$ more completely: $Pb^{++} + SO_4^{--} \rightleftarrows PbSO_4$ solution $\rightleftarrows PbSO_4$ precipitate.

(36) Bismuth.—To the solution reserved from **(35)** add NH_4OH until the mixture is alkaline (outside test on red litmus paper). Centrifuge or filter, wash, and reserve decantate for **(37)**. Confirm the presence of bismuth by adding 1 drop of $NaHSnO_2$ solution [see (**24,** *e*)] to the precipitate. A black color indicates the presence of *bismuth.*

Notes.—1. An excess of NH_4OH is needed to redissolve any basic salts of Cu^{++} and Cd^{++} that might precipitate at this point.

2. Hg^{++}, if not properly separated in **(34)**, will give a white precipitate with NH_4OH and a black precipitate with $NaHSnO_2$ solution.

(37) Copper.—If the solution reserved from **(36)** is blue, the presence of copper is indicated. If the color is indecisive, transfer a few drops to a test tube, acidify with dilute H_2SO_4, and add 1 drop of $K_4Fe(CN)_6$ solution. A rose color indicates the presence of a trace of Cu^{++}. Reserve the remainder of the solution for **(38)**.

Note.—An excess of $K_4Fe(CN)_6$ solution might interfere with the test for Cu^{++} by precipitating yellowish $Cd_2Fe(CN)_6$, which might largely cover up the red color of $Cu_2Fe(CN)_6$.

(38) Cadmium.—If Cu^{++} is absent, saturate the solution from **(37)** with H_2S. A yellow precipitate of CdS indicates the presence of *cadmium.* If Cu^{++} is present, use Method *A* or Method *B* (Instructions).

Sometimes, owing to faulty technique, a black precipitate is obtained. Filter, and treat the residue by Method *A*, below. The interferences are usually due to Ag^+, Pb^{++}, or Bi^{+++}, which were not properly removed in the preceding steps.

A. Hydrogen Sulfide Method.—If Cu^{++} is present, saturate the solution with H_2S, centrifuge, and decant. Add to the residue 2 ml. of dilute H_2SO_4 and heat in a water bath 1 or 2 min. Decant the solution to a flask, alkalize with NH_4OH, and saturate with H_2S. A yellow precipitate of CdS indicates the presence of *cadmium.*

Note.—This separation of Cd^{++} from other members of the Copper subgroup is based upon the preferential solution of CdS in hot dilute H_2SO_4. This difference is based, in turn, upon CdS being more soluble in water than the other sulfides, excepting PbS. H_2SO_4 converts PbS into $PbSO_4$, which is insoluble, and this difference effects its separation also.

B. Cyanide Method.—To the blue solution from **(37)** add NaCN solution drop by drop until the blue color is displaced. Saturate with H_2S. An *immediate* yellow precipitate of CdS indicates cadmium.

Notes.—1. CN^- reacts with Cu^{++}, forming first $Cu(CN)_2$, later breaking down into colorless $Cu_2(CN)_2$ and cyanogen, C_2N_2. The $Cu_2(CN)_2$ reacts with excess CN^- to form a very stable cuprocyanide, undecomposable by H_2S. The C_2N_2 is absorbed by the NH_4OH present.

2. Occasionally, when Cu^{++} is present in large amounts, H_2S reacts with C_2N_2 to form a red precipitate of dithiooxalamide, $C_2S_2(NH_2)_2$. This precipitate is soluble in an excess of warm water, while CdS is insoluble.

TABLE IV.—ANALYSIS OF COPPER SUBGROUP

<table>
<tr><td colspan="4">(34) Residue from $(NH_4)_2S$ extraction: HgS, PbS, Bi_2S_3, CuS, CdS. Add 4 ml. H_2O + 2 ml. dilute HNO_3. Heat to boiling, filter, wash precipitate.</td></tr>
<tr><td rowspan="3">Residue: HgS, S.
Dissolve in aqua regia, filter. Add $SnCl_2$.
Gray precipitate: Hg_2Cl_2-Hg. white-black</td><td colspan="3">(35) Filtrate: Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}. Add H_2SO_4, evaporate to fumes. Dilute, wash precipitate.</td></tr>
<tr><td rowspan="2">Precipitate: $PbSO_4$.
Extract with NaOH. Acidify filtrate with $HC_2H_3O_2$; add $K_2Cr_2O_7$.
Precipitate: $PbCrO_4$ (yellow)</td><td colspan="2">(36) Filtrate: Bi^{+++}, Cu^{++}, Cd^{++}. Add NH_4OH, filter, wash precipitate.</td></tr>
<tr><td>Precipitate: $Bi(OH)_3$.
Add $NaHSnO_2$
Residue: Bi (black).</td><td>(37) Filtrate: $Cu(NH_3)_4^{++}$, $Cd(NH_3)_4^{++}$. If blue, proceed to (38); if indecisive, divide, acidify smaller portion with H_2SO_4, add $K_4Fe(CN)_6$.
Brown precipitate (or rose color): $Cu_2Fe(CN)_6$. If Cu^{++} is found, treat remaining solution by (38, <i>A</i> or <i>B</i>).
(38) <i>A</i>. Saturate with H_2S, centrifuge or filter. Heat residue with dilute H_2SO_4, filter. To filtrate add NH_4OH, H_2S.
Precipitate: CdS (yellow).
(38) <i>B</i>. Decolorize with NaCN; saturate with H_2S.
Precipitate: CdS (yellow).</td></tr>
</table>

(39) Precipitation of the Tin Subgroup.—To the solution reserved from (**33**) add dilute HCl dropwise until the mixture is acid. Warm in the hot-water bath for 2 min. to coagulate the precipitate, and then centrifuge or filter, and discard the solution. A white residue is probably sulfur; a colored residue indicates the presence of the Tin subgroup. Reserve the colored residue for (**40**) or (**43**).

Notes.—1. Sometimes the color of a mixture of Sb_2S_3 and SnS_2 is not a reddish yellow, as would be expected, but brown, or even black. This anomalous color effect has not been explained.

2. Appreciable amounts of Hg^{++} and Cu^{++} sometimes appear in the Tin subgroup. This is due, for the most part, to faulty technique in the separation of the Copper and Tin subgroups. Too much NH_4OH may have been used, or the mixture was not treated with H_2S long enough to convert the NH_3 derivatives of these ions into sulfides. In such cases, a false indication of the presence of the Tin subgroup is given.

Use Method *A* or Method *B* (Instructions).

Method A

(40) Arsenic.—Drain the residue from (**39**) and add 2 ml. (graduate) of concentrated HCl and 2 ml. of alcohol. Stir the mixture and heat it in a water bath at 70° for at least 10 min. Centrifuge or filter, and wash the residue twice with 1 ml. of water. Combine the washings with the main solution and reserve it for (**41**) or (**44**).

Add to the residue 3 ml. of dilute HNO_3 and heat in the hot-water bath until the reaction is complete. Filter out any free sulfur. Transfer the solution to a casserole and evaporate to a paste. Add a drop of $AgNO_3$ solution and 2 or 3 drops of 10 per cent $NH_4C_2H_3O_2$ solution. A chocolate color (due to Ag_3AsO_4) indicates the presence of *arsenic.*

Notes.—1. The basis of this separation is the insolubility of As_2S_3 and As_2S_5 (and HgS) in concentrated HCl. Sb_2S_3, Sb_2S_5, and SnS_2 (and CuS) dissolve readily in this reagent.

2. The mixture is heated to only 70°, since As_2S_5 is somewhat soluble in boiling concentrated HCl. The alcohol is added to reduce this solubility.

3. If Sb_2S_3 or SnS_2 is present there will be a certain amount of effervescence during the early stages of the digestion, owing to the liberation of H_2S formed by their dissolving in the acid.

4. S is removed since it interferes with the Ag_3AsO_4 test. HNO_3 oxidizes S to SO_2, which in turn reduces AsO_4^{---} to AsO_3^{---}. That is, As cannot be oxidized beyond the AsO_3^{---} stage in the presence of S.

5. The HNO_3 treatment converts As_2S_5 into H_3AsO_4 and S: $3As_2S_5 + 10HNO_3 + 4H_2O \rightarrow 2H_3AsO_4 + 15S + 10NO$.

6. The $AgNO_3$-$NH_4C_2H_3O_2$ mixture develops a dark color upon standing, even when As is absent. The formation of Ag_2S, due to the H_2S in the air of the laboratory, is generally the cause.

(41) Antimony.—Evaporate the solution from **(40)** in a casserole to about 2 ml., in order to remove some of the excess HCl. If this evaporation is carried out over an open flame, the alcohol will take fire and will burn harmlessly. This inflammation may be avoided by evaporating over a hot-water bath. Transfer the solution to a test tube, introduce a piece of aluminum wire,[1] and let the reaction run (use a hood) until the Al is completely dissolved. A black curdy residue is metallic antimony (or possibly arsenic, if that element was not properly separated). Decant or filter, and reserve the solution for **(42)**.

If arsenic was found in **(40)**, suspend the black residue in 1 or 2 ml. of water and add 1 drop of 10 per cent NaOH solution and 2 or 3 drops of bromine solution. An insoluble black residue confirms the presence of *antimony.*

Notes.—1. Most of the HCl is removed by evaporation, so that the reaction with Al will not be too vigorous.

2. The reduction of Sb^{+++} to metallic Sb by means of Al should be carried out under a hood. Small amounts of stibine, SbH_3 (and arsine, AsH_3), may be evolved, and these gases are highly poisonous.

3. Metallic As is soluble in sodium hypobromite solution, NaOBr, while Sb is not.

4. Any Cu^{++} carried over from the Copper subgroup will be precipitated by the Al as metallic copper (red).

(42) Tin.—To the clear solution from **(41)** add a few drops of $HgCl_2$ solution. A satin-white precipitate of Hg_2Cl_2 or a gray precipitate of Hg indicates the presence of *tin* in the solution as $SnCl_2$.

Notes.—1. Aluminum reduces Sn^{++++} to the metallic stage, but the latter redissolves in the HCl, forming Sn^{++}.

---

[1] These pieces of Al wire are cut so as to weigh about 0.05 gram each.

2. $SnCl_2$ solutions on standing are oxidized by the air to $SnCl_4$, thus: $2SnCl_2 + 4H^+ + 4Cl^- + O_2 \text{ (air)} \rightarrow 2SnCl_4 + 2H_2O$. For this reason, the $HgCl_2$ test should be made promptly.

Method B

(43) Arsenic.—Follow the procedure in **(40)**.

(44) Antimony.—Dilute the solution from **(43)** to 10 ml. and transfer it to a small Erlenmeyer flask. Place the flask in a beaker of hot water and saturate with H_2S for 5 min. If no precipitate forms, add 1 ml. of water and resaturate with H_2S. Centrifuge or filter while hot and reserve the solution for **(45)**. An orange-red precipitate, insoluble in $(NH_4)_2CO_3$, indicates *antimony*.

TABLE V.—ANALYSIS OF THE TIN SUBGROUP

<table>
<tr><td colspan="4">(39) Solution: AsS_4^{---}, SbS_4^{---}, SnS_3^{--}, S^{--} and S_x^{--}. Acidify with HCl, heat to coagulate precipitate. Extract residue at 70° with 2 ml. of conc. HCl + 2 ml. of alcohol. Centrifuge or filter, wash precipitate.</td></tr>
<tr><td rowspan="6">(40), (43).
Residue: As_2S_{3-5}, S.
Heat with HNO_3, filter out S. Evaporate, add $AgNO_3$, $NH_4C_2H_3O_2$.
Residue: Ag_3AsO_4 (brown)</td><td colspan="3">Solution: Sb^{+++}, Sn^{++++}. Proceed to <i>A</i> or <i>B</i>.</td></tr>
<tr><td colspan="3"><i>A</i>. (41) Boil out excess HCl, add Al.</td></tr>
<tr><td>Residue: Sb (+As) (black). Extract with NaOBr.
Residue: Sb (black).</td><td colspan="2">(42) Solution: Sn^{++}. Add $HgCl_2$.
Precipitate: Hg_2Cl_2 (white), Hg (gray). Sn is indicated.</td></tr>
<tr><td colspan="3"><i>B</i>. (44) Dilute to 10 ml., saturate with H_2S.</td></tr>
<tr><td rowspan="2">Precipitate: Sb_2S_3, (As_2S_5)
Extract with $(NH_4)_2CO_3$.
Residue: Sb_2S_3 (orange).</td><td colspan="2">(45) Solution: Sn^{++++}, (Sb^{+++}). Add Al, warm, filter.</td></tr>
<tr><td>Residue: Sb(?).
Extract with $HNO_3 + H_2C_4H_4O_6$.
Saturate extract with H_2S.
Precipitate: Sb_2S_3 (orange).</td><td>Solution: Sn^{++}. Add $HgCl_2$
Precipitate: Hg_2Cl_2 (white), Hg (gray). Sn is indicated.</td></tr>
</table>

Notes.—1. The above method for separating Sb^{+++} from Sn^{++++} depends upon the fact that Sb_2S_3 is much less soluble than SnS_2 and for that reason can be precipitated from hot HCl solution, in which the latter is soluble.

2. Orange Sb_2S_3 is distinguished from yellow As_2S_3 by the solubility of the latter in $(NH_4)_2CO_3$ solution.

(45) Tin.—To the solution from **(44)**, add a piece of Al wire. A mouse-colored deposit is probably metallic tin. After the Al is all dissolved, heat the mixture in the water bath to redissolve any Sn, filter the solution, and reserve any residue. Add 1 or 2 drops of $HgCl_2$ to the solution. A white precipitate of Hg_2Cl_2 or a gray-black precipitate of Hg indicates the presence of *tin* in the solution.

A black residue remaining after the treatment with Al wire is probably Sb, incompletely precipitated as the sulfide in **(44)**. If Sb has not been found, boil the residue with 1 or 2 ml. of dilute HNO_3 plus 1 or 2 drops of tartaric acid solution, $H_2C_4H_4O_6$. Dilute the solution to 10 ml. and saturate with H_2S. An orange-yellow precipitate confirms the presence of *antimony.*

GROUP III. THE AMMONIUM SULFIDE GROUP

This group consists of the cations whose chlorides are soluble and whose sulfides are not precipitated by H_2S in dilute acid solution (*i.e.*, $0.25M$ HCl), but whose sulfides (or hydroxides) are precipitated by $H_2S + NH_4OH$, *i.e.*, $(NH_4)_2S$, in the presence of NH_4^+ salts. The membership of the group is

THE ALUMINUM SUBGROUP	THE IRON SUBGROUP
Aluminum, Al^{+++}	Manganese, Mn^{++}
Chromium, Cr^{+++}	Iron, Fe^{++} and Fe^{+++}
Zinc, Zn^{++}	Cobalt, Co^{++}
	Nickel, Ni^{++}

Al^{+++} and Cr^{+++} are precipitated as $Al(OH)_3$ and $Cr(OH)_3$, since their sulfides are completely hydrolyzed by water.

The presence of NH_4^+ ions prevents the premature precipitation of Mg^{++} as $Mg(OH)_2$.

The basis for the division into subgroups is the solubility of $Al(OH)_3$, $Cr(OH)_3$, and $Zn(OH)_2$ in $NaOH + Na_2O_2$. $Al(OH)_3$ and $Zn(OH)_2$ are amphoteric, and Na_2O_2 oxidizes $Cr(OH)_3$ to CrO_4^{--}.

PRELIMINARY EXPERIMENTS

(46) Complication by Phosphates and Oxalates. *Precipitation of Group IV Ions and Mg^{++} in Group III.*—Dissolve a pinch of calcium phosphate, $Ca_3(PO_4)_2$ (or calcium oxalate, CaC_2O_4), in a few drops of dilute HCl, dilute, and add NH_4OH as in the precipitation of Group III (?). What is the precipitate? In what group is Ca^{++} normally precipitated?

(47) Aluminum, Al^{+++}. (*a*) *Aluminum Hydroxide.*—Dilute 1 or 2 drops of aluminum sulfate solution, $Al_2(SO_4)_3$, with 2 ml. of water and add NH_4OH (?, E). (SEPARATION OF Al^{+++} FROM CrO_4^{--} AND Zn^{++}.) Centrifuge and reserve the precipitate for (*b*).

Repeat the experiment, using $(NH_4)_2S$ (formed by saturating NH_4OH with H_2S) instead of NH_4OH. Is there any apparent difference in the precipitates?

Note.—$(NH_4)_2S$ solution always contains OH^- ions; *i.e.*, $(NH_4)_2S + H_2O \rightleftarrows 2NH_4OH + H_2S$. Since $Al(OH)_3$ is more insoluble than Al_2S_3, Al^{+++} ions combine with these OH^- ions in preference to the S^{--} ions.

(*b*) *Aluminates.*—Using the precipitate formed in (*a*), test the solubility of $Al(OH)_3$ in NaOH (?). Consider the product to be the metaaluminate, AlO_2^-. Complete the equation, $Al(OH)_3 + OH^- \rightarrow$?

$Al(OH)_3$ is only slightly soluble in NH_4OH. Explain the difference.

What class of hydroxides shows both basic and acid properties?

(*c*) *Lake Formation.*—Dilute 1 drop of $Al_2(SO_4)_3$ to about 2 ml., add 1 drop of "aluminon" solution, and make the solution alkaline with 1 drop of NH_4OH (?). If the solution is yellow instead of red, too much NH_4OH has been added. In this case, add 1 or 2 drops of $NH_4C_2H_3O_2$ to "buffer" the solution, *i.e.*, to reduce its alkalinity. Warm, centrifuge, and note colors of precipitate and solution.

Notes.—1. Aluminon, the trade name for aurin tricarboxyllic acid, is an organic dye and forms a colored precipitate ("lake") with $Al(OH)_3$.

2. A buffer is a salt which tends to neutralize a solution. NH_4^+ ions tend to neutralize bases by combining with the OH^-, forming the very slightly ionized NH_4OH; and $C_2H_3O_2^-$ ions tend to neutralize acids by combining with H^+, forming the slightly ionized $HC_2H_3O_2$. It is seen that $NH_4C_2H_3O_2$ is a buffer for both bases and acids.

(48) Chromium, Cr^{+++}. (*a*) *Chromium Hydroxide.*—Dilute a drop of chromic chloride solution, $CrCl_3$, to 2 ml. and add NH_4OH (?, E). Centrifuge or filter, and reserve the precipitate for (*b*) and (*c*).

Note.—$Cr(OH)_3$ tends to dissolve in excess of NH_4OH, giving a purple solution. This is believed to contain a NH_3-Cr complex ion. [See $Cu(NH_3)_4^{++}$.]

(*b*) *Chromites.*—To a portion of the precipitate reserved from (*a*), add an excess of NaOH (?, E). Consider the solution to contain a metachromite. Dilute and heat in the hot-water bath for several minutes (?, E).

Would you expect $Cr(OH)_3$ to be completely insoluble in an excess of NH_4OH?

(*c*) *Oxidation of $Cr(OH)_3$ to Chromate.*—To the remainder of the $Cr(OH)_3$ precipitate reserved from (*a*), add 1 ml. of water and a pinch of Na_2O_2 (or a few drops each of NaOH and H_2O_2) and heat in the water bath for several minutes (?). Balance the equations:

$$Cr(OH)_3 + Na_2O_2 \rightarrow Na^+ + CrO_4^{--} + OH^- + H_2O$$
$$Cr(OH)_3 + H_2O_2 + OH^- \rightarrow CrO_4^{--} + H_2O$$

Note.—Sodium peroxide should be obtained by the student from the storeroom or side shelf *on a watch glass* and *in small quantity.* Never pour the powder from the can directly into a solution, for moisture from the solution will ruin the supply by causing the can to corrode and the peroxide to decompose. Sodium peroxide is an exceedingly active oxidizing agent, and, when brought in contact with paper, towels, or wood, spontaneous combustion may take place. For this reason, the student is required to throw any excess of the material into the sink (not the waste jars) and to flush it into the drain with plenty of water. Never store it in the desk.

(*d*) *Peroxide Test for Chromate and Dichromate.*—Dilute 1 drop to K_2CrO_4 or $K_2Cr_2O_7$ to 1 ml., add 1 drop of dilute H_2SO_4 or HNO_3, and cover with 1 ml. of ether. Add 1 drop of H_2O_2 solution and mix promptly (?). The blue color is a test for CrO_4^{--} or $Cr_2O_7^{--}$ but is not a test for Cr^{+++}.

(*e*) *Barium Chromate.*—Dilute 1 drop of $K_2Cr_2O_7$ and add 2 drops of $Ba(C_2H_3O_2)_2$ (?, E). (SEPARATION OF CR FROM ZN.) Divide the mixture into two parts. Use one part to test the solubility of $BaCrO_4$ in dilute HNO_3, and the other part to test in $HC_2H_3O_2 + NaC_2H_3O_2$.

(*f*) *Reduction of Dichromate by Hydrogen Sulfide.*—Dilute 2 drops of $K_2Cr_2O_7$ to about 3 ml., acidify with 1 drop of dilute HCl, and saturate with H_2S (?). Heat in the hot-water bath for 1 min., centrifuge, and examine the precipitate (?). Write the equation.

Repeat the experiment, using 2 drops of $K_2Cr_2O_7$ in a solution alkaline with NH_4OH. Note that the reaction is very slow, and the amount of reduction is negligible. CrO_4^{--} must previously be reduced to Cr^{+++} (*e.g.*, by H_2S in Group II) in order for Cr to be found in Group III.

(49) Zinc, Zn^{++}. (*a*) *Solubility of Zinc Hydroxide in Ammonium Hydroxide and in Sodium Hydroxide Solutions.*—Dilute 1 drop of zinc nitrate solution, $Zn(NO_3)_2$, to about 1 ml. and add NH_4OH, at first drop by drop (E), then in excess (E). (SEPARATION OF Zn^{++} FROM Al^{+++}.)

Repeat, using NaOH solution instead of NH_4OH, noting similar effects (E's).

Does $Zn(OH)_2$ behave as an acid in both cases?

What would be the probable action of water on ammonium zincate, $(NH_4)_2ZnO_2$ (E)?

Note.—The solubility of $Zn(OH)_2$ in excess NH_4OH is due to the formation of the complex ion $Zn(NH_3)_4^{++}$, which gives too low a concentration of Zn^{++} ions for $Zn(OH)_2$ to be precipitated even by strong bases like NaOH. It does, however, afford a high enough concentration of Zn^{++} ions for the complete precipitation of ZnS. This depends on the fact that the concentration of the S^{--} ions may be large in alkaline solutions, since the H^+ ions are almost wholly absent.

(*b*) *Solubility of Zinc Sulfide.*—Place 1 or 2 drops of $Zn(NO_3)_2$ solution in a small Erlenmeyer flask, dilute to a convenient volume, and add colorless ammonium sulfide—*i.e.*, add NH_4OH until the mixture clears and then saturate with H_2S (E). What is the color of ZnS? Shake and divide the mixture into three portions. To one add dilute HCl in slight excess (?). To the second, add $HC_2H_3O_2$ (?). To the third, add about 1 ml. of sodium acetate solution and a few drops of dilute HCl (?).

Note.—The precipitation of ZnS depends wholly upon the presence in the solution of sufficient numbers of Zn^{++} and S^{--} ions. If a precipitate fails to form, it is because one of these ions (S^{--}, usually) is present in exceedingly small amount. Other ions have no effect except as they increase or diminish the number of these ions. ZnS does not form in the presence of strong acids, like HCl, because the large number of H^+ ions from the strong acid drives back the ionization of the H_2S, thus: $2H^+ + S^{--} \rightleftarrows H_2S$ (the "common ion effect"). On the other hand, if the salt of a weak acid like acetic acid is present, the anions of this weak acid will combine with the H^+ ions of the strong acid, removing them with practical completeness. This permits an increased ionization of the H_2S with the result that the S^{--} ions become numerous enough to precipitate the Zn^{++} ions as ZnS.

(50) Manganese, Mn^{++}. (*a*) *Manganous Hydroxide.*—Dilute 1 or 2 drops of manganous nitrate solution, $Mn(NO_3)_2$, with freshly boiled water and add a drop of NaOH (E). Note that $Mn(OH)_2$ is white. Transfer the mixture to a casserole and swirl in contact with the air (?, E).

Mix 1 or 2 drops of $Mn(NO_3)_2$ with 5 drops of NH_4NO_3 and add 2 drops of NH_4OH (?). Can $Mn(OH)_2$ be precipitated in the presence of NH_4^+ salts?

Note.—The failure of $Mn(OH)_2$ to form in the presence of NH_4^+ salts is usually explained as due to the repression of the OH^- ions by excess NH_4^+ (common ion effect). [See $Mg(OH)_2$, page 74.]

(*b*) *Manganese Dioxide.*—Place 1 or 2 drops of $Mn(NO_3)_2$ in a test tube and add 1 ml. of concentrated HNO_3 and a single small crystal of $KClO_3$. Warm the mixture in a hot-water bath (?). (SEPARATION OF Mn^{++} FROM Fe^{+++}, Co^{++}, Ni^{++}.) Complete the equation: $Mn^{++} + HClO_3 + H_2O \rightarrow MnO_2 + H^+ + HCl$. (The actual reaction is more complicated than this simple equation represents. $HClO_4$, ClO_2, and Cl_2 are also formed.)

Try the solubility of a small amount of MnO_2 in dilute HNO_3 in a casserole or beaker (?). Now add to the mixture a few drops of $NaNO_2$ solution (?). Complete and balance the equation: $MnO_2 + NO_2^- + H^+ \rightarrow Mn^{++} + NO_3^-$, etc. What kind of reagent is NO_2^- in this reaction?

Repeat the experiment, using H_2O_2 instead of $NaNO_2$ solution (?). What is the gas evolved? Complete the equation, $MnO_2 + H_2O_2 + H^+ \rightarrow$?

(*c*) *Oxidation of Mn^{++} and MnO_2 to MnO_4^-.*—Mix a pinch of MnO_2 and equal amount of $NaBiO_3$ and add 1 ml. of dilute HNO_3. Heat in the hot-water bath for 2 min. The rose color in the solution is due to MnO_4^-. Balance the equation: $MnO_2 + BiO_3^- + H^+ \rightarrow MnO_4^- + Bi^{+++} + H_2O$.

(51) Iron: Fe^{++} and Fe^{+++}. (*a*) *Colors of Ions.*—In general, what are the colors of solutions of (1) ferrous and (2) ferric salts?

(*b*) *Hydroxides.*—Dilute 1 drop of ferrous sulfate solution, $FeSO_4$, with 2 ml. of freshly boiled water and add 1 drop of NaOH solution (?, E). Divide the mixture into two parts. Pour one part into a casserole and swirl it in contact with air (?, E). To the other part add H_2O_2 (?, E).

Note.—Pure $Fe(OH)_2$ is white. Upon oxidation it shows a number of colors—green, black, and finally brown.

Dilute 1 or 2 drops of ferric chloride solution, $FeCl_3$, and add NH_4OH (?, E). Is the precipitate soluble in excess NH_4OH? (SEPARATION OF FE FROM CO AND NI.)

(*c*) *Sulfides.*—Dilute 1 drop of $FeSO_4$ solution and add $(NH_4)_2S$ solution (*i.e.*, $NH_4OH + H_2S$) (?, E). Compare the general appearances of FeS and Fe_2S_3 (?).

Note.—The precipitate obtained when $(NH_4)_2S$ is added to a Fe^{+++} solution is Fe_2S_3 and not FeS, as formerly represented. When Fe_2S_3 is dissolved in non-oxidizing acid, the product is Fe^{++} ions, owing to the reducing action of H_2S on Fe^{+++}.

(*d*) *Reduction of Fe^{+++} to Fe^{++}.*—Dilute 2 drops of $FeCl_3$ to about 3 ml., add 1 or 2 drops of dilute HCl, and saturate with H_2S (?, E). Note the turbidity of the mixture (?). Complete the equation, $Fe^{+++} + H_2S \rightarrow ? + ? + ?$. What kind of reagent is H_2S in this reaction?

(*e*) *Oxidation of Fe^{++} to Fe^{+++}.*—Dilute 2 drops of $FeSO_4$ and add 3 drops of dilute HCl and 1 drop of dilute HNO_3. Heat in a hot-water bath (?, E).

(*f*) *Tests for Fe^{++} and Fe^{+++}.*—Dilute 2 or 3 drops of $FeSO_4$ solution to about 3 ml. and divide the solution into three portions. Test these portions with 1 drop each of NH_4SCN, $K_4Fe(CN)_6$, and $K_3Fe(CN)_6$, respectively.

Repeat the experiment, using $FeCl_3$ instead of $FeSO_4$.

Arrange your results in a table, thus:

REAGENTS	FE^{++}	FE^{+++}
SCN^-	....	....
$Fe(CN)_6^{----}$	....	....
$Fe(CN)_6^{---}$	....	....

What impurity is responsible for the positive reactions of the Fe^{++} solution with SCN^- and $Fe(CN)_6^{----}$? In the second and third columns, check the reactions that seem to be specific for the ion in question. How would you test for Fe^{+++} and Fe^{++} in a solution containing both?

Notes.—1. The product of the reaction between Fe^{+++} and $Fe(CN)_6^{----}$ is commonly called "Prussian blue" and is represented by the formula $Fe_4(Fe(CN)_6)_3$. The product of the reaction between Fe^{++} and $Fe(CN)_6^{---}$ is "Turnbull's blue" and is represented by the formula $Fe_3(Fe(CN)_6)_2$. The constitutions of these substances do not seem to be definite but are, rather, approximations.

2. The reaction of NH_4SCN with Fe^{+++} solutions depends upon the formation of the complex ion, $Fe(SCN)_6^{---}$. This ion is fairly stable, and the test may be made in the presence of considerable amounts of HCl without appreciable loss in sensitiveness. This is due to the fact that HSCN is a highly ionized acid, and therefore the presence of the H^+ ions from the HCl reduces the concentration of the SCN^- to only a slight extent.

Dilute 1 drop of NH_4SCN to about 1 ml. and add 1 or 2 drops of concentrated HNO_3 (?). Heat the mixture to boiling (?). Is a red color with NH_4SCN an infallible test for Fe^{+++}?

Note.—The products in the reaction between SCN^- and HNO_3 are not definitely known. A number of products have been detected, *e.g.*, NO, NO_2, CO_2, COS, SO_4^{--}, etc. No equation need be written.

(52) Cobalt, Co^{++}. (*a*) *Colors of Cobalt Ions.*—To 1 drop of cobalt nitrate solution, $Co(NO_3)_2$, in a casserole, add 2 drops of concentrated HCl (?). If there is no change in color, evaporate in a casserole. Complete the equation: $Co(H_2O)_6^{++}$ (pink) + heat → ?. What kind of reagent is HCl in this case?

(*b*) *Cobalt-Ammonia Complex Ion.*—Dilute 1 or 2 drops of $Co(NO_3)_2$ to about 1 ml. and add NH_4OH drop by drop. Note two stages in the reaction (?, E's). Reserve the solution for the next experiment.

Note.—The general rule for the composition of metal-ammonia complex ions is that the number of NH_3 molecules is twice the valence of the metal, *e.g.*, $Ag(NH_3)_2^+$, $Cu(NH_3)_4^{++}$, etc. Divalent cobalt and nickel are exceptions in that they form several complexes, with 6 NH_3 molecules as the upper limit. The general usage is to represent them by the formulas $Co(NH_3)_6^{++}$ and $Ni(NH_3)_6^{++}$.

(*c*) *Cobalt Sulfide.*—Saturate the solution reserved from the preceding experiment with H_2S (?, E). [Consider the reaction as between $Co(NH_3)_6^{++}$ and H_2S.] Centrifuge or filter, and try the solubility of the precipitate in dilute HCl (?) and in dilute aqua regia (?).

Note.—It is anomalous that HCl should prevent the precipitation of CoS and yet CoS should be insoluble in HCl. Some authorities consider CoS to be really soluble but believe that the action is *very slow*.

(*d*) *Cobalt Hydroxides.*—Dilute 1 or 2 drops of $Co(NO_3)_2$ to about 2 ml. and add 1 or 2 drops of NaOH (?, E). Now add a little Na_2O_2, or 2 drops of H_2O_2 solution, and warm the mixture (?). Does Co resemble Fe or Ni in this respect?

(*e*) *Thiocyanate Reaction.*—Dilute 1 drop of $Co(NO_3)_2$ solution with 4 or 5 drops of water and add 1 drop of NH_4SCN solution and then 1 ml. of a mixture of amyl alcohol and ether (?).

Repeat the experiment, diluting the $Co(NO_3)_2$-NH_4SCN mixture to 3 or 4 ml. before adding the alcohol-ether mixture (?). What condition is necessary for the formation of the blue-green solution?

(*f*) *Reaction with Dimethylglyoxime.*—Dilute 1 drop of $Co(NO_3)_2$ solution to 1 ml., neutralize any free acid with a drop of NH_4OH, and add a drop of dimethylglyoxime solution (?). The composition of the brown substance is not known.

(53) Nickel, Ni^{++}. (*a*) *Color of Nickel Ions.*—To a drop of nickel nitrate solution, $Ni(NO_3)_2$, in a casserole, add 2 drops of concentrated HCl and evaporate nearly to dryness. Is there any apparent change in color? [See $Co(H_2O)_6^{++}$, page 50.]

(*b*) *Nickel-Ammonia Complex Ion.*—Dilute 1 drop of $Ni(NO_3)_2$ to 1 ml. and add NH_4OH, noting two stages in the reaction (?, E). What other complex ammonia ion resembles this one in color? Reserve the solution for the next experiment.

(*c*) *Nickel Sulfide.*—Dilute the solution reserved from (*b*) and saturate it with H_2S (?, E). Centrifuge the resulting solution, wash the precipitate, and reject the decantate. Try the solubility of NiS in (1) dilute HCl (?) and (2) dilute aqua regia (?, E).

Mix 1 drop of $Ni(NO_3)_2$ solution with 2 drops of yellow ammonium sulfide, $(NH_4)_2S_x$, and dilute to about 2 ml. Can the precipitate be separated by means of filtration or centrifugation? Acidify with dilute HCl or $HC_2H_3O_2$ and warm (?, E).

(*d*) *Nickel Hydroxide.*—Dilute 1 drop of $Ni(NO_3)_2$ to about 1 ml. and add 1 drop of NaOH solution (?, E). Add a little Na_2O_2

or 1 or 2 drops of H_2O_2. Can $Ni(OH)_2$ be easily oxidized to $Ni(OH)_3$?

(*e*) *Reaction with Dimethylglyoxime.*—Dilute 1 drop of $Ni(NO_3)_2$ to 1 ml., neutralize any free acid with a drop of NH_4OH, and add a drop of dimethylglyoxime solution (?).

Note.—Dimethylglyoxime is an organic compound with the empirical formula $C_4H_8N_2O_2$. It functions as a weak monobasic acid, forming the red nickel salt $Ni(C_4H_7N_2O_2)_2$.

Exercises

1. What members of Group III could be present in a solution containing free NH_4OH?
2. What members of Group III form amphoteric hydroxides?
3. What two members of Group III are precipitated by the group reagents as hydroxides? What is their valence?
4. What members of Group III are absent if NH_4OH gives no reaction (precipitate or color) with the H_2S-free solution?
5. What hydroxides of Group III are oxidized by Na_2O_2 in alkaline solution? What hydroxides (or oxides) are reduced by H_2O_2 in acid solution?
6. Do the trivalent metals form carbonates? Why?
7. How would the following behave if exposed to the air: (*a*) saturated H_2S solution, (*b*) moist MnS, (*c*) colorless $(NH_4)_2S$, (*d*) moist $Mn(OH)_2$, (*e*) $FeCl_2$ solution.
8. What reagent will separate NiS and FeS in one step?
9. What members of this group form black sulfides?
10. What cation of this group gives with NH_4OH a white precipitate soluble in excess of the reagent?
11. What members of this group form NH_3 complexes?
12. Refer to the Table of Solubilities (pages 148–151) and find a cation belonging to a group subsequent to Group III which forms a sulfide insoluble in water. Why is not this ion a member of Group III?
13. Why is $Mn(OH)_2$ not precipitated by NH_4OH in the presence of NH_4^+?
14. What members of this group form sulfides insoluble in dilute HCl?
15. Why should yellow ammonium sulfide, $(NH_4)_2S_x$, never be used in the analysis of Group III?
16. What ion gives no reaction with NH_4OH in the presence of NH_4Cl but upon standing in contact with the air develops a brown precipitate?
17. What non-metallic substance resembling $Al(OH)_3$ is sometimes met in this group? How may it be distinguished from $Al(OH)_3$?
18. How would you go about separating the ions Al^{+++}, Zn^{++}, and Ni^{++}, by means of NaOH and NH_4OH?
19. A solution is known to be either $Al_2(SO_4)_3$ or $ZnSO_4$. What test would you make?

20. Which is the more powerful oxidizing agent, $HMnO_4$ or $NaBiO_3$ in the presence of HNO_3?

21. Molar solutions of HCl and $HC_2H_3O_2$ are saturated with H_2S. Compare the concentrations of the S^{--} ion in the two cases.

22. Explain why the addition of a soluble acetate increases the S^{--} concentration in acid solutions containing H_2S.

23. A Group III solution gives with NH_4OH a deep-blue solution over a reddish-brown precipitate. What ions are indicated?

24. Apply the rules of hydrolysis to NH_4AlO_2 and $FePO_4$.

25. Using NH_4OH, how could $Cr_2(SO_4)_3$ and $NiSO_4$ be distinguished?

26. Indicate reagents and products (see page 33 for form in answers) in the following one-step separations:

(*a*) Al^{+++} and Zn^{++}.
(*b*) $Cr(OH)_3$ and $Fe(OH)_3$.
(*c*) Co^{++} and Mn^{++}.
(*d*) Zn^{++} and Ni^{++}.
(*e*) CoS and FeS.
(*f*) $Fe(OH)_3$ and $Ni(OH)_2$.
(*g*) CrO_4^{--} and Zn^{++}.

27. State what, if anything, would be formed in the following cases. Do not balance equations.

(*a*) $Cr_2O_7^{--} + H_2S + H^+ \rightarrow$
(*b*) $Fe^{+++} + H_2S \rightarrow$
(*c*) $Cr^{+++} + CO_3^{--} + H_2O \rightarrow$
(*d*) $Zn(NH_3)_4^{++} + H^+ \rightarrow$
(*e*) $Zn^{++} + H_2S + Ac^-$ (excess) →
(*f*) $Fe(OH)_3$ + NaOH solution →
(*g*) $Mn(OH)_2$ + air →
(*h*) MnO_2 + conc. HNO_3 →
(*i*) $MnO_4^- + Pb^{++} + H^+ \rightarrow$
(*j*) $Fe^{+++} + Fe(CN)_6^{----} \rightarrow$
(*k*) $Co(SCN)_2$ in ether + H_2O →
(*l*) $Ni(OH)_2 + Na_2O_2 \rightarrow$

28. Criticize the following definition of Group III: "Group III contains those cations whose sulfides (or hydroxides) are insoluble in water but soluble in dilute acids."

29. Why is the H_2S in the filtrate from Group II boiled out before starting on the precipitation of Group III?

30. Try to name some anions other than PO_4^{---} and $C_2O_4^{--}$ which, if not removed, would precipitate Group IV and Mg^{++} in Group III.

31. Why is a large excess of NH_4OH to be avoided in the precipitation of $Al(OH)_3$?

32. What hydroxides of Group III are amphoteric?

33. A Group III solution gives no precipitate with excess of NH_4OH. The absence of what ions is indicated?

34. A Group III solution gives with excess NH_4OH no reaction, and with $NH_4OH + H_2S$ a white precipitate. Interpret.

35. A Group III solution gives no precipitate upon treatment with $NaOH + Na_2O_2$. Interpret.

36. Explain how excess Na_2O_2 is removed from an alkaline solution. Write equation.

37. How could you distinguish between zinc sulfide and white precipitated sulfur?

ANALYSIS

(**54**) **Complication by Phosphate and Oxalate.**—The procedure to be followed in Group III, particularly in the Iron subgroup, is determined by the presence or absence of PO_4^{---} and $C_2O_4^{--}$ ions. Upon adding NH_4OH to solutions containing these anions, Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++} are precipitated as insoluble phosphates and oxalates.[1] In order to recover these members of Groups IV and V, these interfering anions are removed during the course of the Group III analysis, and the Group III precipitation is repeated, at least in part. This calls for a longer and more involved procedure, which should be used only when necessary. Therefore, before starting the analysis, the student should ascertain whether these complicating anions are present or absent. (Instructions.)

Test for Oxalate.—This test is made on the original unknown, using a pinch of a solid or 2 or 3 drops of a solution. Place the sample in a test tube or a small flask and acidify with 0.5 ml. of dilute H_2SO_4. Disregard any precipitate. Heat in the water bath until the mixture ceases to effervesce. Cool the solution under the tap and add dilute $KMnO_4$ solution until the purple color persists. Promptly connect the tube or flask [see (**103**), page 92, for apparatus to be used] with a tube or trap containing $Ca(OH)_2$ solution. Heat in a hot-water bath to drive over all the gas evolved. The formation of a white precipitate of $CaCO_3$ indicates the presence of *oxalate*. Sometimes this precipitate is dissolved by excess of the gas.

---

[1] Borates and fluorides would also precipitate the members of Group IV, but these anions have presumably been removed by the HNO_3 evaporation in (**30**).

Note.—The effervescence is usually due to decomposition of carbonates. If not previously removed, the CO_3^{--} ion would spoil the test for $C_2O_4^{--}$ H_2S and SO_2 may also be expelled during the heating.

Test for Phosphate.—Use a pinch of a solid or 2 or 3 drops of a solution, if the substance is an original unknown. If the substance is a filtrate from a Group II precipitation, use a 1-ml. sample, reserving the remainder of the solution for (**55**). Place the sample in a casserole, add 1 ml. of concentrated HNO_3, and evaporate almost to dryness. Take up the residue in 1 ml. of dilute HNO_3 and transfer the solution to a test tube. Add 1 ml. of the ammonium molybdate reagent and heat for 1 min. in a hot-water bath. A yellow precipitate of $(NH_4)_3PO_4.12MoO_3$ indicates the presence of *phosphate.*

Notes.—1. The ammonium molybdate reagent is prepared by dissolving $(NH_4)_2MoO_4$ in HNO_3 and really consists of H_2MoO_4 and NH_4NO_3 in excess HNO_3. H_2MoO_4 is unstable, and the solution tends to break down, forming a precipitate of molybdic anhydride. Consequently, a H_2MoO_4 solution containing a precipitate should be regarded with suspicion and should be tested from time to time with a PO_4^{---} solution (*e.g.*, Na_2HPO_4).

2. H_2S and other strong reducing agents interfere with the test by forming with the molybdate reagent a suspension of "molybdenum blue." These interferences are destroyed by the preliminary evaporation with HNO_3.

3. An excess of Cl^- ions reduces the sensitiveness of the test.

4. In general unknowns, the test for PO_4^{---} is made on the filtrate from Group II rather than on the original solution. AsO_4^{---} ions give a yellow precipitate with the $(NH_4)_2MoO_4$ reagent, identical in appearance with the phosphate precipitate. The test is therefore deferred until after As is removed.

(**55**) **Precipitation.**—Proceed according to *A* or *B*, depending on the nature of the unknown.

A. The Substance Is an Unknown of Group III Only.—If the substance is a solid, dissolve a pinch in 2 ml. of dilute HCl and dilute to about 5 ml. in a small Erlenmeyer flask; if the substance is a solution, acidify a 0.5-ml. portion with a few drops of dilute HCl and dilute to 5 ml. Saturate the solution with H_2S, filter out any sulfur precipitate, and proceed to *B*.

Note.—Since chromium must be in the Cr^{+++} form in order to be precipitated in Group III, the solution is put through the precipitation-by-H_2S procedure of Group II. This reduces CrO_4^{--} (yellow) to Cr^{+++} (green), MnO_4^- (purple) to Mn^{++} (faint pink), and Fe^{+++} (yellow-brown) to Fe^{++} (faint green). Furthermore, the neutralization of the HCl by NH_4OH

provides sufficient NH_4^+ salts to prevent the precipitation of $Mg(OH)_2$ in this group.

B. The Solution Is a Filtrate from Group II or from A Above.—Boil gently the solution reserved from (**31**) and (**54**) for 1 min. to remove H_2S and add NH_4OH drop by drop until precipitation is complete. Note and interpret the appearance of the mixture. Without filtering, saturate with H_2S and interpret all changes. Filter or decant, and wash the precipitate promptly with hot water. Reserve the precipitate for (**56**), and the filtrate (and first washings) for (**72**).

Notes.—1. The H_2S from the Group II precipitation is boiled out, so that the effect of NH_4OH alone on the solution may be noted. Considerable time may be saved by taking advantage of information obtained in this way.

2. The filtrate from Group II already contains NH_4Cl in sufficient amount to prevent the precipitation of ordinary amounts of $Mg(OH)_2$, $Ca(OH)_2$, etc. This was formed by the neutralization of the dilute HCl added in the precipitation of Group I by the NH_4OH added above.

3. The reaction of NH_4OH with Group III solutions gives very valuable information. Failure to give any reaction (color or precipitate) indicates the absence of all ions of the group except Zn^{++} and possibly Mn^{++}. A clear blue color indicates the presence of Ni^{++} a clear brown, Co^{++}. A white gelatinous precipitate suggests Al^{+++}; and a green precipitate, Cr^{+++} or Fe^{++}; a reddish-brown precipitate, Fe^{+++}; and a dirty-brown precipitate, Mn^{++}.

4. Yellow ammonium sulfide, $(NH_4)_2S_x$, must not be used in the analysis of Group III because of its solvent action on NiS. $NH_4OH + H_2S$ is used instead.

5. If moist sulfides are allowed to stand in contact with the air, sulfate is formed by oxidation and will dissolve in the wash water. For this reason, the precipitate should be washed promptly with hot (free from dissolved air) water.

(**56**) **Separation into Subgroups.**—By means of a jet of water from a wash bottle, transfer the precipitate from (**55**) to a small beaker and add concentrated HCl drop by drop as long as there is any visible reaction. If a black residue remains (suggesting what substances?), warm the mixture and add concentrated HNO_3 (1 or 2 drops is usually enough) until solution is complete. Filter and reject any residue (sulfur). Evaporate the filtrate in a casserole to 2 or 3 ml., and dilute to about 10 ml. Add NaOH solution until the mixture is distinctly alkaline and add a pinch of Na_2O_2 (Instructions).

If PO_4^{---} and $C_2O_4^{--}$ have been found present, add 1 ml. of Na_2CO_3 solution. This will convert $BaCrO_4$ and $SrCrO_4$ into carbonates, so as to leave the CrO_4^{--} ion in the solution of the Aluminum subgroup.

A colored precipitate indicates the presence of the Iron subgroup and possibly Group IV and Mg^{++}. A white precipitate may be $FePO_4$ or insoluble salts of Group IV and Mg^{++}. If no precipitate forms, the Iron subgroup, as well as phosphates and oxalates of succeeding groups, is absent.

Evaporate the alkaline solution to a small volume. Dilute to 10 ml. and centrifuge or filter, and reserve the solution for **(57)** and the precipitate for **(60)**.

TABLE VI.—PRECIPITATION OF GROUP III AND SEPARATION INTO SUBGROUPS

<table>
<tr><td colspan="3">**(54)** Test a portion of the *original* substance for $C_2O_4^{--}$ by means of $KMnO_4$ and test a portion of the filtrate from Group II for PO_4^{---} by means of the $(NH_4)_2MoO_4$ reagent. Proceed to *A* or *B*.
(55) *A. The Solution Is an Unknown of Group III Only.*—Acidify with HCl, saturate with H_2S, and filter out any S. Proceed to *B*.
B. The Solution Is a Filtrate from Group II.—Boil out H_2S; add NH_4OH. Precipitate: $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_{2-3}$; also phosphates and oxalates of Group III, Group IV, and Mg^{++}, if these ions are present. Without filtering, saturate with H_2S, centrifuge or filter, and wash.</td></tr>
<tr><td colspan="2">**(56)** Precipitate: $Al(OH)_3$, $Cr(OH)_3$, ZnS, MnS, FeS, Fe_2S_3, CoS, NiS; also Group IV and Mg^{++} as phosphates and oxalates. Add concentrated HCl. Dissolve any black residue (CoS, NiS) in HNO_3. Reject any S. Add NaOH, Na_2O_2, and Na_2CO_3 (if PO_4^{---} and $C_2O_4^{--}$ may be present). Boil, centrifuge or filter, wash precipitate.</td><td rowspan="2">Filtrate: Groups IV, V. See Table IX or X.</td></tr>
<tr><td>Solution: AlO_2^-, CrO_4^{--}, $HZnO_2^-$. See Table VII.</td><td>Precipitate: MnO_2, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$; also Group IV and Mg^{++} as phosphates, oxalates, and carbonates. See Table VIII.</td></tr>
</table>

Notes.—1. Again, proper observation and interpretation of the colors of precipitates and solutions formed may give valuable information. It may also suggest how the procedure may be shortened without risk of error.

2. The Na_2O_2 causes the following oxidations: green $Cr(OH)_3$ into yellow CrO_4^{--}, white $Mn(OH)_2$ into black MnO_2, green-to-white $Fe(OH)_2$ to brown $Fe(OH)_3$, and pink $Co(OH)_2$ into black $Co(OH)_3$.

3. Effervescence (due to $2Na_2O_2 + 2H_2O \rightarrow 4Na^+ + 4OH^- + O_2$) does not necessarily indicate an excess of the reagent. On the other hand, large excesses must be avoided, since enough Fe^{+++} will be carried into the Aluminum subgroup to give a positive test for Al^{+++} with the aluminon reagent.

4. An important effect of the boiling of the alkaline solution is the decomposition of the excess of Na_2O_2. If this excess is not removed, it will be changed into H_2O_2 upon acidification, and the latter will subsequently react with H_2S, giving white S. The latter may be mistaken for a test for zinc [see (**59**)].

(**57**) **Aluminum.**—Concentrate the solution from (**56**) to about 2 ml. in a beaker or casserole and carefully acidify it with dilute HCl. Then alkalize it with a few drops of NH_4OH and heat in a hot-water bath for 1 min. Centrifuge or filter, wash, and reserve the solution for (**58**). A white gelatinous precipitate of $Al(OH)_3$ indicates *aluminum.*

If the identity of the precipitate is questionable, dissolve it in 1 or 2 drops of dilute HCl and add 1 drop of the "aluminon" reagent and 1 ml. of $NH_4C_2H_3O_2$. Heat in a water bath for a short time and centrifuge. A red lake confirms the presence of *aluminum.*

Notes.—1. A large excess of NH_4OH must not be used in the precipitation of $Al(OH)_3$, since, owing to its amphoteric properties, $Al(OH)_3$ is somewhat soluble in NH_4OH.

2. Traces of Al^{+++} are introduced into unknowns from the glassware and porcelain. The student should learn to distinguish between these traces and large amounts.

3. Excess of "aluminon" should be avoided, since it is hard to see a red precipitate in a red solution. If a red precipitate does not separate, either centrifuge and decant, leaving a red residue, or filter and wash, leaving a red precipitate on the paper.

(**58**) **Chromium.**—If the solution from (**57**) is yellow, chromium is present in the form of the CrO_4^{--} ion. If the color is not decisive, concentrate the solution to 2 ml., transfer a drop (use a pipette) to a test tube, and add a drop of H_2O_2 solution and 0.5 ml. of ether, acidifying with dilute H_2SO_4. Shake promptly. A blue color in the ether layer confirms the presence of *chromium.*

If CrO_4^{--} ions are present, heat the solution to boiling and add $Ba(C_2H_3O_2)_2$ drop by drop as long as a precipitate continues to form. Centrifuge, decant, and reserve the solution for (**59**).

Notes.—1. Occasionally the solution is yellow owing to such reasons as these: (1) Organic matter was not completely removed in (**30**); and (2) polysulfides were formed by failure to filter out the sulfur formed upon acidifying the solution with HNO_3 in (**56**). These reasons make it desirable to carry out the H_2O_2 confirmatory test in most cases.

2. The presence of H_2O_2 (from Na_2O_2) or other reducing agent will interfere with the "perchromic acid" test by previously reducing $Cr_2O_7^{--}$ to Cr^{+++}, which will not give a blue color.

3. The solution is boiled, since $BaCrO_4$ settles better when precipitated from hot solution.

4. In almost every case, even in the absence of CrO_4^{--}, a white precipitate is formed with $Ba(C_2H_3O_2)_2$. This seems to be due to SO_4^{--} formed by the oxidation of sulfides and sulfur by the air and Na_2O_2.

(59) Zinc.—Saturate the solution reserved from (**58**) with H_2S. A white precipitate of ZnS, insoluble in $HC_2H_3O_2$ but soluble in HCl, indicates *zinc.*

Notes.—1. Oxidizing agents, such as H_2O_2 and $H_2Cr_2O_7$, should be completely removed before making the H_2S test for Zn^{++}. Oxidizing agents form with H_2S a white precipitate of sulfur.

2. If there is doubt whether any of the precipitate dissolved in the HCl, then centrifuge or filter, neutralize the filtrate with NH_4OH, and resaturate with H_2S. A white precipitate is confirmatory.

TABLE VII.—ANALYSIS OF ALUMINUM SUBGROUP

<table>
<tr><td colspan="2">(57) Solution: AlO_2^-, CrO_4^{--}, $HZnO_2^-$. Evaporate to 2 ml. acidify and alkalize with NH_4OH. Warm, centrifuge, wash precipitate.</td></tr>
<tr><td rowspan="2">Precipitate: $Al(OH)_3$.
Confirm by dissolving in HCl and adding "aluminon," NH_4OH, and $NH_4C_2H_3O_2$. Red lake indicates Al.</td><td>(58) Solution: CrO_4^{--} (yellow), $Zn(NH_3)_4^{++}$. Concentrate, and test a drop with H_2O_2, ether, and H_2SO_4. A blue color indicates the presence of CrO_4^{--}. If CrO_4^{--} is present, add $Ba(C_2H_3O_2)_2$ to the remainder of the solution, centrifuge, wash, and reject the precipitate.</td></tr>
<tr><td>(59) Solution: $Zn(NH_3)_4^{++}$. Saturate with H_2S. White precipitate: ZnS.</td></tr>
</table>

(60) Manganese.—Place the residue from (**56**) in a small casserole, add a few drops of concentrated HNO_3, and warm the mixture. If solution is not complete (due to what?), add 1 drop of $NaNO_2$ solution. Evaporate to a volume of about 1 ml. and add another milliliter of concentrated HNO_3. Heat almost to boiling and slowly add powdered $KClO_3$, using in all an amount about equal to a large grain of rice. Heat on the water bath at least 1 min. A brown-to-black precipitate of MnO_2 indicates *manganese.* Dilute with a little water, centrifuge, and wash the precipitate. Reserve the solution for (**61**) or (**64**).

It is customary to confirm this test by adding to the precipitate a pinch of $NaBiO_3$ and 2 ml. of dilute HNO_3 and heating the mixture in the water bath for several minutes. A rose color in the solution, due to MnO_4^-, confirms the presence of manganese.

Notes.—1. The black residue, insoluble in HNO_3, is MnO_2 or $Co(OH)_3$ or both. This residue is seldom encountered, since generally there is present enough H_2O_2, formed from the excess Na_2O_2, to reduce these substances to Mn^{++} and Co^{++}, respectively. Oxides of nitrogen, dissolved in the HNO_3, have the same effect.

2. The $KClO_3$ reacts with the concentrated HNO_3, forming chloric acid, $HClO_3$. The $HClO_3$ molecules, and not the ClO_3^- ions, seem to be the active oxidizing agent. Therefore, in the equilibrium $HClO_3 \rightleftarrows H^+ + ClO_3^-$, excess of H^+ ions from the concentrated HNO_3 favors more rapid oxidation.

3. The presence of filter paper, or other reducing agent, will hinder or completely prevent the formation of the MnO_2 precipitate.

4. The MnO_2 is best separated by centrifugation. Filtration is possible only through non-reducing media, as a layer of asbestos supported in a funnel by a plug of glass wool.

5. Brown stains of MnO_2 may be removed from glassware and porcelain by means of dilute HNO_3 and H_2O_2 or $NaNO_2$ solution.

Procedure in the Absence of Phosphate and Oxalate

If PO_4^{---} and $C_2O_4^{--}$ have been found to be present in (**54**), proceed directly to (**64**). If both were absent, proceed as follows:

(**61**) **Iron.**—Add to the solution reserved from (**60**) 1 ml. of concentrated HCl and evaporate to 2 ml. This removes the excesses of HNO_3 and $KClO_3$ which would interfere with the confirmatory tests for Fe^{+++}. Add NH_4OH in slight excess and heat in the hot-water bath for 1 min. Centrifuge or filter, and wash the precipitate. A red-brown precipitate of $Fe(OH)_3$ indicates the presence of *iron.* Divide the solution into two parts and reserve them for (**62**) and (**63**).

The presence of Fe^{+++} may be confirmed as follows: Dissolve the precipitate in a few drops of dilute HCl, dilute to 1 ml., and divide the solution into two portions. To the first portion add 1 drop of NH_4SCN solution; a blood-red color is due to $Fe_2(SCN)_6$. To the second portion add $K_4Fe(CN)_6$ solution; the formation of a precipitate of Prussian blue likewise confirms the presence of Fe^{+++}.

Notes.—1. The amount of the $Fe(OH)_3$ precipitate should be noted. A small amount may be due to contamination by iron in the water or in certain of the reagents, or to dust from the ironware of the apparatus. For this test to have any significance, care must be taken to protect the solutions from this ubiquitous element.

2. If the separation from Co^{++} and Ni^{++} has not been complete, these elements will interfere more or less with the ferrocyanide test. Co^{++} will give a bluish precipitate of $Co_2Fe(CN)_6$, and Ni^{++} a green precipitate of $Ni_2Fe(CN)_6$.

3. Nitrates interfere by forming a pink color with NH_4SCN. This color fades out on standing. Since HNO_3 and NH_4SCN mutually destroy each other, an excess of the latter is used to insure the formation of $Fe_2(SCN)_6$.

4. Occasionally, owing to failure to allow time enough for the MnO_2 to precipitate completely in (**60**), a brown precipitate of hydrated MnO_2 appears at this point. Aside from the possible failure to detect Mn, this causes no complication, for $Mn_2Fe(CN)_6$ is soluble in dilute HCl, and $Mn(SCN)_2$ is colorless.

(**62**) **Cobalt.**—Acidify one portion of the solution reserved from (**61**) with a few drops of concentrated HCl and evaporate to 1 ml. Add 1 drop of NH_4SCN solution and about 0.5 ml. of a mixture of amyl alcohol and ether, and centrifuge. A blue-green color in the alcohol-ether layer indicates the presence of *cobalt.*

Notes.—1. The presence of Co^{++} is generally indicated long before the SCN^- test is made. A pink solution [due to the hydrated ion, $Co(H_2O)_6{}^{++}$], changing upon concentration to a blue solution (due to $CoCl_4{}^{--}$), is a sufficient test for cobalt.

2. The composition of the blue-to-green thiocyanate is not positively known. The latest proposal is that it is due to the complex ion $Co(SCN)_4{}^{--}$. Upon dilution, the color reverts to pink. It follows that the thiocyanate test cannot be made on dilute solutions.

3. If through faulty work all the Fe^{+++} ions were not removed on (**61**), a red color will be formed in the alcohol-ether layer, covering any blue color of the Co^{++} complex. If only a trace of Fe^{+++} is present, this interference can be obviated by adding a pinch of sodium potassium tartrate, $NaKC_4H_4O_6$, which converts the red $Fe_2(SCN)_6$ into a colorless ferric tartrate. Large amounts of Fe^{+++} require a repetition of (**61**).

(**63**) **Nickel.**—By the dropwise addition of $HC_2H_3O_2$, acidify the second portion of the solution reserved from (**61**) and add 1 drop of dimethylglyoxime solution. A red precipitate indicates the presence of *nickel.* A brown solution or filtrate is due to cobalt.

Procedure in the Presence of Phosphate and Oxalate

Oxalate ions, if present in the original, have now been removed by oxidation with $HClO_3$ in (**60**). However, this removal did not take place in time to prevent $C_2O_4^{--}$ ions carrying Ba^{++}, Sr^{++}, and Ca^{++} into Group III. Proper steps must therefore be taken to separate these Group IV ions and make tests for them.

(**64**) **Iron.**—To a few drops of the solution reserved from (**60**), add 3 or 4 drops of concentrated HCl and evaporate almost to dryness in a casserole. Take up the residue in a little water plus 1 or 2 drops of dilute HCl and divide the solution into two parts. Test these parts for Fe^{+++} by $K_4Fe(CN)_6$ and by NH_4SCN, as in (**61**).

(**65**) **Removal of Phosphate.**—To the remainder of the filtrate from (**60**) add $FeCl_3$ solution until the solution shows a distinctly yellow color. Now add NH_4OH drop by drop until a precipitate which will not dissolve upon shaking just forms. Carefully redissolve the precipitate in the minimum amount of $HC_2H_3O_2$. Add 2 ml. of 50 per cent $NH_4C_2H_3O_2$ solution. If the mixture is not reddish, add more $FeCl_3$ and repeat the procedure. Dilute to 30 ml. and heat in the water bath for 2 or 3 min. Filter the mixture while hot. Add a little NH_4OH to the filtrate and heat again in the water bath to insure complete precipitation of Fe^{+++} compounds. Reject all precipitates. Reserve the filtrate for (**66**).

Notes.—1. The purpose of the above procedure is the separation of PO_4^{---} from the divalent cations: Ni^{++}, Co^{++}, Ba^{++}, Sr^{++}, Ca^{++}, and Mg^{++}. Advantage is taken of the fact that Fe^{+++} forms the phosphate of least solubility, so that all of this anion combines with Fe^{+++}, forming $FePO_4$. Any excess Fe^{+++} is then precipitated as $Fe(OH)_2C_2H_3O_2$, leaving the divalent ions in solution.

2. The hydrolysis of $Fe(C_2H_3O_2)_3$ may be represented by $Fe(C_2H_3O_2)_3 + 2H_2O + \text{heat} \rightleftarrows Fe(OH)_2C_2H_3O_2 + 2HC_2H_3O_2$. It appears then that both dilution and heat favor the formation of the basic salt.

(**66**) **Separation of Co^{++} and Ni^{++} from Groups IV and V.**—Saturate the ammoniacal solution from (**65**) with H_2S, centrifuge or filter, and wash the precipitate, which may contain CoS or NiS, or both. Combine the first washings with the main filtrate and reserve for (**67**). Transfer the precipitate to a casserole and dissolve it in dilute HCl plus 1 or 2 drops of concentrated HNO_3. Filter out the residue (S, mainly) and evaporate the solution to a volume of 1 or 2 ml. Note any color effects during the concentration. Divide the solution and test one portion of it for Co^{++} by (**62**) and test the other portion for Ni^{++} by (**63**).

Note—A sufficient test for Co^{++} is the color change from pink to blue during the evaporation.

(**67**) **Removal of Excess Ammonium Salts.**—Evaporate the solution from the H_2S precipitation in (**66**) to dryness in a casserole, add 1 drop of concentrated HNO_3, and evaporate again. Finally, ignite the residue as long as a gas seems to be given off. Take up the residue in 2 ml. of water plus a drop of concentrated HCl, warm, and centrifuge (or filter) if necessary. Test the solution for Group IV and Mg^{++} by (**72**) and subsequent procedures.

Note.—The purpose of the evaporation with HNO_3 is to convert all ammonium salts into NH_4NO_3, which is decomposed into N_2O and H_2O by the subsequent ignition. Unless ammonium salts are removed in this way, they may completely prevent the precipitation of Group IV in (**72**). Compare (**72**, note 2).

It should be noted that there are now two solutions that may contain Groups IV and V, *viz.*, (1) the filtrate from (**55**)—the regular filtrate from Group III, and (2) the solution just prepared. These solutions *must not be combined*, since the latter contains Na^+, introduced in the NaOH, Na_2O_2, and Na_2CO_3 reagents in (**56**), and K^+ introduced as $KClO_3$ in the Mn^{++} precipitation in (**60**). Mixing, it will be seen, would spoil the tests for both Na^+ and K^+ in Group V. Furthermore, both solutions must be analyzed. Frequently, all of a cation goes into one or the other of these solutions. On the other hand, the two Group IV precipitates may be combined and analyzed together.

TABLE VIII.—ANALYSIS OF IRON SUBGROUP

<table>
<tr><td colspan="4">(60) Residue: MnO_2, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$; also phosphates, oxalates, and carbonates of Group IV and Mg^{++}. Add conc. HNO_3, boil. If residue remains, add $NaNO_2$. Concentrate, heat with conc. $HNO_3 + KClO_3$. Centrifuge, wash precipitate.</td></tr>
<tr><td rowspan="7">Precipitate: Black MnO_2.
Confirm by adding $HNO_3 + NaBiO_3$.
Purple solution: MnO_4^-.</td><td colspan="3">If PO_4^{---} or $C_2O_4^{--}$ is present, proceed to (64); if absent, follow (61).</td></tr>
<tr><td colspan="3">(61) Solution: Fe^{+++}, Co^{++}, Ni^{++}. Add HCl, evaporate, add NH_4OH, centrifuge or filter, wash precipitate.</td></tr>
<tr><td rowspan="2">Precipitate: Brown $Fe(OH)_3$. To confirm, dissolve in HCl and divide solution. To one part add NH_4SCN. Blood-red solution: $Fe_2(SCN)_6$. To other part add $K_4Fe(CN)_6$. Blue precipitate: $Fe_4(Fe(CN)_6)_3$.</td><td colspan="2">Solution: $Co(NH_3)_6^{++}$, $Ni(NH_3)_6^{++}$. Divide and test by (62) and (63).</td></tr>
<tr><td>(62) Acidify one part with HCl, evaporate. Add NH_4SCN, amyl alcohol-ether, centrifuge.
Blue layer: $Co(SCN)_4^{--}$.</td><td>(63) Acidify second part with $HC_2H_3O_2$, add dimethylglyoxime.
Red precipitate: Ni-dimethylglyoxime.</td></tr>
<tr><td colspan="3">(64) Solution: Fe^{+++}, Co^{++}, Ni^{++}, Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}. Test a small portion of the solution for Fe^{+++} by NH_4SCN or $K_4Fe(CN)_6$. (65) If PO_4^{---} is present, add $FeCl_3$, NH_4OH, $HC_2H_3O_2$, $NH_4C_2H_3O_2$, boil, centrifuge or filter, wash precipitate.</td></tr>
<tr><td rowspan="2">Precipitate: $FePO_4$, $Fe(OH)_2C_2H_3O_2$.
Discard.</td><td colspan="2">(66) Solution: Co^{++}, Ni^{++}, Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, NH_4^+. Saturate with H_2S, centrifuge or filter, wash precipitate.</td></tr>
<tr><td>Precipitate: Black CoS, NiS. Dissolve in $HCl + HNO_3$, add NH_4OH, and test by (62) and (63).</td><td>(67) Filtrate: Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, NH_4^+. Evaporate to dryness, add HNO_3, ignite. Residue: Group IV, Mg^{++}. Dissolve in H_2O, HCl, and proceed to Tables IX, X.</td></tr>
</table>

GROUP IV. THE AMMONIUM CARBONATE GROUP

This group contains the cations of the alkaline earth metals:

Calcium, Ca^{++}.
Strontium, Sr^{++}.
Barium, Ba^{++}.

The chlorides of these metals are soluble in water, and their sulfides and hydroxides are not precipitated in the presence of NH_4^+ salts.

The most uniformly insoluble salt of the group is the carbonate, and hence the group is precipitated in this form. The group reagent is ammonium carbonate, $(NH_4)_2CO_3$. A sufficient concentration of NH_4^+ ions is maintained to prevent the precipitation of $MgCO_3$.

In the analysis, Ba^{++} ions are precipitated as the chromate, since $BaCrO_4$ shows the greatest solubility difference from the corresponding Sr^{++} and Ca^{++} compounds. Sr^{++} may be separated from Ca^{++} by the direct precipitation of $SrCrO_4$ in ammoniacal solution in the presence of alcohol. An alternative procedure is the detection of these ions more or less in the presence of each other, based upon certain differences in solubility.

The following table shows the solubility in *moles per liter* of the compounds which are involved in the separation and analysis of the group:

SOLUBILITY TABLE

	Ba^{++}	Sr^{++}	Ca^{++}	Mg^{++}
CO_3^{--}	0.00009	0.00004	0.0001	0.005
CrO_4^{--}	0.000015	0.006	1	3
SO_4^{--}	0.00001	0.0005	0.0078	2.8
$C_2O_4^{--}$	0.0004	0.00024	0.00005	0.009
$(OH)_2^{--}$	0.22	0.065	0.022	0.00014

PRELIMINARY EXPERIMENTS

(68) Precipitation of the Group.—Dilute 1 drop of barium nitrate solution, $Ba(NO_3)_2$, used as a representative of the group, to 1 ml. and add 1 or 2 drops of ammonium carbonate solution,

$(NH_4)_2CO_3$ (E). Mix well and heat in the hot-water bath for 5 min. Centrifuge or allow the mixture to stand until the precipitate has settled. Decant and try the solubility of the precipitate in warm $HC_2H_3O_2$ (?, E).

√*Note.*—Contrary to the probable opinion of the student at this point, chemical reactions in solutions are by no means instantaneous. It is characteristic of the precipitates of this group to form slowly, especially from dilute solutions. Heating and shaking may hasten such reactions to some extent, but the wiser policy is always to allow the mixtures to stand until the precipitation is complete, *i.e.*, the precipitate is "digested" (see page 7) in the mother solution. Heating such a digestion mixture favors the formation of large-grained particles, which are more easily filtered, and is valuable in this way. Instead of waiting for these slow reactions to complete themselves, the student should proceed with other work, *e.g.*, the preliminary experiments on Group V.

(69) Barium, Ba^{++}. (*a*) *Reaction with Sulfate Ions.*—Dilute 1 drop of $Ba(NO_3)_2$ solution to about 1 ml. and add 1 drop of dilute H_2SO_4 (E). Centrifuge (or allow to stand until the precipitate has settled) and decant the solution. Try the solubility of this precipitate in a strong acid, *e.g.*, dilute HCl (?). Reserve the residue for (*c*) below.

To another drop of $Ba(NO_3)_2$ add about 1 drop of water and 2 or 3 drops of saturated $CaSO_4$ solution (?, E). What would happen if saturated $BaSO_4$ solution was added to $Ca(NO_3)_2$ solution? Explain the difference.

(*b*) *Precipitation of Barium Chromate.*—Dilute 1 drop of $Ba(NO_3)_2$ solution to about 1 ml. and add 1 drop of $K_2Cr_2O_7$ (E). (SEPARATION OF BA^{++} FROM SR^{++} AND CA^{++}.) Settle this precipitate by standing or centrifuging and decant the solution. Try the solubility of the salt in (1) dilute $HC_2H_3O_2$ and (2) a strong acid (*e.g.*, dilute HCl).

(*c*) *Flame Test.*—Clean a platinum wire by dipping it in HCl solution and heating until the flame color is only a momentary flash. Now dip the wire in $BaCl_2$ solution (on a watch glass) and hold it in the side of a Bunsen flame. Note the color of the flame (?).

Transfer the $BaSO_4$ precipitate reserved from (*c*) to a watch glass. Moisten it with a drop of concentrated HCl and try its flame reaction (?).

Notes.—1. The following is recommended for platinum wires to be used in flame tests: A piece of platinum wire about 6 cm. long is sealed into the end of a short piece of glass tubing (Instructions). A good way to protect the wire against rough usage in the drawer of the desk is to insert the glass tubing into a perforated cork and keep it in a test tube as shown in Fig. 12.

2. The flame coloration is much more conspicuous if the wire is held horizontally in the outer cone near the base of the flame, and the "layer" of coloration observed "edgewise."

3. Non-volatile barium compounds give little or no flame reaction.

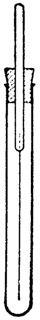

FIG. 12.—Platinum wire in a test tube.

(70) Strontium, Sr^{++}. (*a*) *Strontium Sulfate.*—Dilute 1 drop of strontium nitrate, $Sr(NO_3)_2$, to about 1 ml. and add 1 drop of dilute H_2SO_4 (E). Shake or centrifuge, and let the solution stand 10 min.

Repeat the experiment, using $CaSO_4$ solution instead of H_2SO_4 (?). Which precipitates the faster, $BaSO_4$ or $SrSO_4$? How does the speed of precipitation vary with the concentration of the SO_4^{--} ion?

(*b*) *Flame Test.*—Make a flame test on a little $Sr(NO_3)_2$ solution (?).

(*c*) *Relative Solubilities of Strontium Sulfate and Strontium Oxalate.*—Dilute 1 drop of $Sr(NO_3)_2$ solution to 2 ml. and add 2 drops of $(NH_4)_2SO_4$ solution (a slight excess). (PARTIAL SEPARATION OF SR^{++} FROM CA^{++}.) Filter or centrifuge at once and add 2 drops of ammonium oxalate solution, $(NH_4)_2C_2O_4$, to the filtrate (E). Is such a large precipitate to be expected from the Solubility Table on page 65?

Repeat the experiment, warming the mixture and allowing it to stand several minutes before filtering or centrifuging. (Other work may be tried in the meantime.) Filter and add $(NH_4)_2C_2O_4$ as before (?). What conditions favor the complete precipitation of Sr^{++} as $SrSO_4$ (?). Try the solubility of the SrC_2O_4 precipitate in warm dilute $HC_2H_3O_2$ (?).

(*d*) *Strontium Chromate.*—Dilute 1 drop of $Sr(NO_3)_2$ to 1 ml. and add 1 or 2 drops of $K_2Cr_2O_7$ solution. If a precipitate forms, cautiously dissolve it in $HC_2H_3O_2$. To the clear solution, add NH_4OH in excess and an equal volume of alcohol (?, E). (SEPA-

RATION OF Sr^{++} FROM Ca^{++}.) Filter (or centrifuge and decant) the solution.

(*e*) *Flame Test.*—Make a flame test on 1 drop of $Sr(NO_3)_2$ solution (?). Now dilute the drop with 9 drops of water and repeat the test. Compare the color with that of undiluted $Ca(NO_3)_2$ solution (?). Can Sr^{++} and Ca^{++} be distinguished by their flame tests?

(71) Calcium, Ca^{++}. (*a*) *Relative Solubility of Sulfate and Oxalate.*—Dilute 1 drop of calcium chloride solution, $CaCl_2$, to about 1 ml. and add 1 or 2 drops of ammonium sulfate solution, $(NH_4)_2SO_4$. Shake well and allow the mixture to stand at least 5 min. for the reaction to complete itself (E). Decant or filter, and add 1 drop of NH_4OH (to neutralize any free acid in the $CaCl_2$ solution) and then 1 or 2 drops of $(NH_4)_2C_2O_4$ solution (E). Is Ca^{++} completely precipitated by SO_4^{--}? (See table, page 65). Decant the solution and try the solubility of the CaC_2O_4 precipitate, first in $HC_2H_3O_2$ (?) and then in HCl (E).

Note.—The solubility of CaC_2O_4 in HCl and insolubility in $HC_2H_3O_2$ are due to differences in strength in the acids involved. HCl is almost completely ionized, $H_2C_2O_4$ is ionized about 20 per cent, and $HC_2H_3O_2$ is ionized less than 1 per cent. Now CaC_2O_4 is very slightly soluble in water, and the dissolved portion may be regarded as practically completely ionized. Neglecting the dissolved molecules, the condition may be represented by the equilibrium:

$$CaC_2O_4 \text{ (solid)} \rightleftarrows Ca^{++} + C_2O_4^{--}$$

If an acid is added to such a mixture, then there will be a tendency for the H^+ ions to combine with $C_2O_4^{--}$ ions to form un-ionized molecules of $H_2C_2O_4$, depending upon the amount of H^+ ions present. Such a reaction will shift the equilibrium to the right, resulting in the solution of undissolved CaC_2O_4. The effect will be very large in the case of HCl, owing to the high concentration of H^+ present, but almost negligible in the case of $HC_2H_3O_2$, where the concentration of H^+ is quite small. SrC_2O_4, on the other hand, is more soluble than CaC_2O_4 and therefore gives a higher concentration of $C_2O_4^{--}$ ions—high enough to react with the H^+ ions from $HC_2H_3O_2$.

(*b*) *The Flame Test.*—Make a flame test on a little $CaCl_2$ solution (?). Would it be easy to distinguish between small amounts of Ca^{++} and Sr^{++} by means of this test?

Exercises

1. By what other names is Group IV known?
2. What salt of Group IV is most uniformly insoluble?
3. What ion is the actual precipitant for Group IV cations?
4. The filtrate from Group III sometimes contains a large amount of NH_4^+ ions. How does this excess of NH_4^+ ions affect the precipitation of Group IV?
5. Why is Group IV precipitated from a hot solution?
6. Is the formation of the Group IV precipitate an instantaneous reaction?
7. What change takes place in a Group IV precipitate when it is digested in its "mother liquor"?
8. Explain the solubility of $CaCO_3$ in boiling NH_4Cl solution.
9. Is $Ca(OH)_2$ a very soluble substance? Then why was it not precipitated in Group III?
10. What anion is most suitable for separating Ba^{++} and Sr^{++}?
11. What is the function of the $NaC_2H_3O_2$ when $BaCrO_4$ is precipitated from $Ba(NO_3)_2$ by $K_2Cr_2O_7$ in the presence of $NaC_2H_3O_2$?
12. Name a Group IV salt that is disposed to form supersaturated solutions.
13. Would you expect a precipitate of $SrCrO_4$ to form when equal volumes of M $Sr(NO_3)_3$ and M K_2CrO_4 are mixed?
14. Can $BaSO_4$ be precipitated from $BaCl_2$ solution by a saturated solution of $SrSO_4$?
15. Can Ca^{++} be tested by $(NH_4)_2C_2O_4$ in the presence of Ba^{++} and Sr^{++}?
16. What is the requisite condition for the complete precipitation of Ba^{++} by $K_2Cr_2O_7$ solution?
17. A Group IV solution gives a precipitate with $(NH_4)_2CO_3$ solution but none with $CaSO_4$ solution. What ion is indicated?
18. Does the addition of $NaC_2H_3O_2$ increase or decrease the solubility of $BaCrO_4$ in $HC_2H_3O_2$ solution? Why?
19. What ions and molecules are present in a solution of $(NH_4)_2CO_3$? Express by equilibrium.
20. Why is CaC_2O_4 soluble in HCl but not in $HC_2H_3O_2$?
21. Why is the filtrate from Group III acidified and boiled before precipitating Group IV? Furthermore, why is the solution concentrated?

ANALYSIS

(72) Precipitation.—Proceed according to *A* or *B*, depending upon the nature of the solution.

A. The Solution Is an Unknown Containing Group IV Only.—Dilute 0.5 ml. of the solution to 2 ml., add 2 or 3 drops of NH_4Cl solution, make alkaline with 2 drops of NH_4OH, and heat almost to boiling. To the hot solution add $(NH_4)_2CO_3$ solution slowly until precipitation is complete. Heat the tube in a water bath for several minutes, holding the temperature below the boiling point of the mixture. Allow the mixture to cool. If the precipitate is crystalline and settles well, it may be washed by centrifugation and decantation; if it does not settle well, filtration is necessary.

B. The Unknown Is a Filtrate from Group III.—Acidify the solution with $HC_2H_3O_2$ and evaporate it in a casserole to a volume of not more than 10 ml. Filter out any residue (sulfur, usually) and wash the residue with a few drops of water, adding the washings to the main filtrate. If the residue is dark, and if Ni^{++} has not been detected, extract with dilute aqua regia and evaporate the solution almost to dryness. Dilute with a little water and test for Ni^{++} with 1 or 2 drops of NH_4OH and dimethylglyoxime.

Transfer the solution to a test tube, neutralize with NH_4OH, and precipitate Group IV with $(NH_4)_2CO_3$, as in *A*. Centrifuge or filter, and analyze the precipitate by (**73**) or (**76**). (Instructions.) Reserve the filtrate for (**83**) and subsequent procedures.

Notes.—1. NH_4Cl is added to original Group IV solutions to provide the requisite NH_4^+ concentration to prevent the precipitation of $Mg(OH)_2$ by NH_4OH. No NH_4^+ is added to filtrates from Group III, since sufficient NH_4^+ has been introduced in neutralizing the acid added in Group II.

2. A large excess of NH_4^+ must be avoided, on account of the solvent action on alkaline earth carbonates. For example, $CaCO_3 + 2NH_4^+ \rightleftarrows Ca^{++} + (NH_4)_2CO_3$.

3. Alkaline earth carbonates when precipitated from cold solutions are flocculent and hard to filter; when precipitated from hot solutions they are crystalline and filter well.

Method A

(**73**) **Barium.**—Dissolve the precipitate from (**72**) in 2 drops of dilute $HC_2H_3O_2$ plus 1 ml. of water, warming the mixture if necessary. In case the precipitate is on a filter paper, pour the warm acid through the paper several times until solution is complete and wash with a little water. Heat the solution in a water bath and add 2 drops of $NH_4C_2H_3O_2$ and K_2CrO_4 in slight excess. Filter or centrifuge, wash, and reserve the solution for (**74**). A yellow precipitate, insoluble in $HC_2H_3O_2$, indicates *barium* or a large amount of strontium. Reserve this precipitate until after the test for strontium (**74**) has been made. If strontium is found, dissolve the precipitate in the smallest amount of dilute HCl (2 or 3 drops, usually) and add 1 ml. of $NH_4C_2H_3O_2$ solution. Shake well and let stand for 1 min. A yellow precipitate is a positive indication of *barium.*

Notes.—1. $BaCrO_4$ is colloidal and hard to filter unless it is precipitated from hot solutions.

2. The presence of $SrCrO_4$ in the $BaCrO_4$ precipitate is infrequent. The most common cause of this complication is the use of too large a sample of the unknown for analysis.

3. In the confirmatory test for Ba^{++}, the $NH_4C_2H_3O_2$ buffers the HCl, reducing the concentration of H^+ to a value which will permit the precipitation of $BaCrO_4$ but not of $SrCrO_4$. Most of the Sr^{++} was separated in the first precipitation, and the amount left in the solution at this point is small.

(74) Strontium.—Test a portion of the solution from **(73)** for Sr^{++} by means of a few drops of saturated $CaSO_4$ solution. A white precipitate of $SrSO_4$, forming slowly upon centrifuging or warming, indicates the presence of *strontium.*

If Sr^{++} is found, add, in slight excess, $(NH_4)_2SO_4$ to the remainder of the solution and heat the mixture to almost boiling. Stopper the tube and let it stand 1 hr. or more (preferably overnight) to complete the precipitation. Filter or centrifuge, and reserve the filtrate for **(75)**.

If Sr^{++} is not present, omit the $(NH_4)_2SO_4$ treatment, and proceed directly to **(75)**.

Notes.—1. The presence of orange $Cr_2O_7^{--}$ does not interfere with the $CaSO_4$ test for Sr^{++}. The turbidity caused by a $SrSO_4$ precipitate is easily visible.

2. $SrSO_4$ precipitates slowly. Warming hastens the reaction, but it is necessary to let the reaction mixture stand for some time to reduce the concentration of Sr^{++} to a value at which it will not give a precipitate with the $C_2O_4^{--}$ ion, used in the test for Ca^{++}.

(75) Calcium.—Neutralize the solution reserved from **(74)** with a little NH_4OH, and add 1 or 2 drops of $(NH_4)_2C_2O_4$ solution. A white precipitate of CaC_2O_4 indicates the presence of *calcium.*

Note.—The presence of CrO_4^{--} does not interfere with the $C_2O_4^{--}$ test for Ca^{++}. In alkaline solution, CrO_4^{--} does not oxidize $C_2O_4^{--}$, even upon boiling.

TABLE IX.—ANALYSIS OF GROUP IV
(Method A)

<table>
<tr><td colspan="3">(**72**) Solution: Ba^{++}, Sr^{++}, Ca^{++}, possibly Group V. If the solution is a filtrate from Group III, acidify with $HC_2H_3O_2$, evaporate, and filter out any residue (S, NiS, etc.). If the solution contains Group IV only, add NH_4Cl. To the solutions thus obtained, add NH_4OH, heat, and add $(NH_4)_2CO_3$. Centrifuge or filter, wash precipitate.</td></tr>
<tr><td colspan="2">Precipitate: $\underline{BaCO_3}$, $\underline{SrCO_3}$, $\underline{CaCO_3}$. (**73**) Dissolve in $HC_2H_3O_2$, add $NH_4C_2H_3O_2$, K_2CrO_4. Centrifuge or filter, wash precipitate.</td><td rowspan="2">Filtrate: Group V. See Table XI.</td></tr>
<tr><td>Yellow precipitate: $\underline{BaCrO_4}$ $(+SrCrO_4)$.
If Sr^{++} is found, dissolve in HCl, add $NH_4C_2H_3O_2$.
Precipitate: $\underline{BaCrO_4}$.</td><td>(**74**) Filtrate: Sr^{++}, Ca^{++}. To portion of filtrate add saturated $CaSO_4$.
White precipitate: $\underline{SrSO_4}$.
If Sr^{++} is found, add $(NH_4)_2SO_4$, heat, and let stand. Centrifuge or filter, reject precipitate.
(**75**) Neutralize filtrate with NH_4OH, add $(NH_4)_2C_2O_4$.
White precipitate: $\underline{CaC_2O_4}$.</td></tr>
</table>

Method B

(**76**) **Barium.**—Proceed according to (**73**). Reserve the filtrate from the $BaCrO_4$ precipitation for (**77**).

(**77**) **Strontium.**—Neutralize the solution from (**76**) with a few drops of NH_4OH and add a volume of alcohol equal to that of the solution. If the solution does not show a decided yellow color, add more K_2CrO_4 solution. Digest for several minutes in the water bath. Do not allow the mixture to boil, for that would reduce the concentration of the alcohol. Filter. If the filtrate is not clear, refilter through the same paper. A yellow precipitate indicates *strontium*. Wash with 50 per cent alcohol and reserve the filtrate for (**78**).

Notes.—1. The concentration of the CrO_4^{--} ions is increased by adding a base: $Cr_2O_7^{--}$ (or $2HCrO_4^-$) $+ 2NH_4OH \rightarrow 2CrO_4^{--} + 2NH_4^+ + H_2O$. In this way the solubility product of $SrCrO_4$ is exceeded.

2. $SrCrO_4$ is slightly soluble in water but practically insoluble in 50 per cent alcohol.

3. Freshly precipitated $SrCrO_4$ is colloidal and tends to "run through the paper." Upon digestion at a high temperature, it filters fairly well.

No confirmatory test for Sr^{++} is proposed. The flame test might be made as follows: The precipitate is dissolved in concentrated HCl and the solution evaporated almost to dryness, giving a mixture of $SrCl_2$ and $CrCl_3$: $2SrCrO_4 + 16H^+ + 6Cl^- \rightarrow 2Sr^{++} + 2Cr^{+++} + 8H_2O + 3Cl_2$. The color of the flame, however, is usually yellowish, owing to the difficulty of removing Na^+ and Ca^{++}.

(78) Calcium.—Test the solution reserved from **(77)** for Ca^{++} with $(NH_4)_2C_2O_4$, according to **(75)**.

Table X.—Analysis of Group IV
(Method B)

<table>
<tr><td colspan="3">(72) Solution: Ba^{++}, Sr^{++}, Ca^{++}, possibly Group V. If the solution is a filtrate from Group III, acidify with $HC_2H_3O_2$, evaporate, and filter out any residue (S, NiS, etc.). If the solution contains Group IV only, add NH_4Cl.
To the solutions thus obtained, add NH_4OH, heat, and add $(NH_4)_2CO_3$. Centrifuge or filter, wash precipitate.</td></tr>
<tr><td colspan="2">Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$. (76) Dissolve in $HC_2H_3O_2$, add $NH_4C_2H_3O_2$, K_2CrO_4. Centrifuge or filter, wash precipitate.</td><td rowspan="2">Filtrate: Group V. See Table XI.</td></tr>
<tr><td>Yellow precipitate: $BaCrO_4$ ($+SrCrO_4$).
If Sr^{++} is found, dissolve in HCl, add $NH_4C_2H_3O_2$.
Precipitate: $BaCrO_4$.</td><td>(77) Filtrate: Sr^{++}, Ca^{++}. Add NH_4OH and alcohol. Yellow precipitate: $SrCrO_4$.
(78) Neutralize filtrate with NH_4OH, add $(NH_4)_2C_2O_4$. White precipitate: CaC_2O_4.</td></tr>
</table>

GROUP V. THE SOLUBLE GROUP

This group contains the cations not precipitated in the preceding groups; *i.e.*, it contains those cations whose chlorides, sulfides, hydroxides, and carbonates are soluble in water or in NH_4^+ salt solutions. The membership of the group is

Sodium, Na^+.
Potassium, K^+.
Ammonium, NH_4^+.
Magnesium, Mg^{++}.

There is no group reagent that will precipitate these ions as a group.

This group is called "The Soluble Group" because its salts are characterized by marked solubility, particularly in water containing NH_4^+ salts. On account of the presence of the ions of the alkali metals, potassium and sodium, the group is sometimes called "The Alkali Group." In view of the presence of magnesium, which is quite different in its chemical nature from the alkali metals, this name seems hardly as appropriate as the first one.

PRELIMINARY EXPERIMENTS

(79) Magnesium, Mg^{++}. (*a*) *Magnesium Hydroxide.*—Dilute 1 or 2 drops of magnesium nitrate solution, $Mg(NO_3)_2$, to about 2 ml. and add 1 drop of *clear* NaOH solution (?, E). $Mg(OH)_2$ is one of the most insoluble of the magnesium compounds.

Note.—NaOH solution is sometimes dreggy, owing to the presence of disintegrated glass from the bottle. This suspension resembles $Mg(OH)_2$ in appearance and must be removed by filtration before using.

Dilute 1 or 2 drops of $Mg(NO_3)_2$ solution and add 1 drop of clear NH_4OH (?, E). Now add NH_4NO_3 solution, drop by drop, until the solution is clear. Express the reaction by a reversible equation. (SEPARATION OF Mg^{++} FROM GROUPS III AND IV.)

Note.—The solubility of $Mg(OH)_2$ in NH_4^+ salt solutions is usually explained in terms of the common ion effect. The concentration of the OH^- ion is repressed by the excess of NH_4^+ ions to the point that the solubility product of $Mg(OH)_2$ is not reached. Hence no precipitate forms.

(*b*) *Magnesium Carbonate.*—Dilute a drop of $Mg(NO_3)_2$ and add 1 drop of Na_2CO_3 solution (?, E). To the mixture add NH_4NO_3 solution slowly, shaking after each drop, until the precipitate disappears. Complete the equilibrium: $MgCO_3 + NH_4^+ \rightleftarrows ? + ?$.

Note.—In effect, $(NH_4)_2CO_3$ is a weak electrolyte, and in the presence of an excess of NH_4^+ ions its ionization is repressed, so that the concentration of CO_3^{--} is too small to give a precipitate with the Mg^{++} ions.

(*c*) *Lake Formation.*—Dilute 1 drop of $Mg(NO_3)_2$ solution, add 1 drop of *p*-nitrobenzeneazoresorcinol solution ("S. and O.

reagent"), and make the mixture alkaline with 0.1 per cent NaOH (?). Shake or centrifuge, to coagulate the precipitate.

Note.—NH_4^+ salts interfere with this reaction and must be removed beforehand by ignition.

(*d*) *Magnesium Ammonium Phosphate.*—Dilute 1 drop of $Mg(NO_3)_2$ and add 1 drop each of NH_4Cl solution and *clear* disodium phosphate solution, Na_2HPO_4. Now add NH_4OH dropwise to slight alkalinity and mix well. The precipitate is $MgNH_4PO_4$ (E).

Notes.—1. The NH_4OH and Na_2HPO_4 solutions should be filtered if they are not clear.

2. The NH_4^+ of the NH_4Cl does not appear in the equation for the formation of $MgNH_4PO_4$. Its purpose is to prevent the precipitation of $Mg(OH)_2$.

3. $MgNH_4PO_4$ is readily hydrolyzed into gelatinous $MgHPO_4$, and for that reason it is precipitated from concentrated, rather than dilute, solutions. Furthermore, $MgNH_4PO_4$ is more insoluble than $MgHPO_4$, and the test is more sensitive when made in concentrated solutions.

(80) Potassium, K^+. (*a*) *Flame Test.*—Clean a platinum wire as in (**69,** *c*) and try the flame test with potassium chloride solution, KCl (?). Repeat the test, observing the flame through a cobalt glass. Note the color (?). Is it the same as that observed without the cobalt glass?

Mix a drop of NaCl solution with a drop of KCl solution on a watch glass and make the flame test (1) without the cobalt glass and (2) with the glass (?). What color is absorbed by the cobalt glass?

(*b*) *Potassium Perchlorate.*—Dilute 1 drop of KCl solution to 1 ml. and add 3 or 4 drops of zinc perchlorate solution, $Zn(ClO_4)_2$ (E). If no precipitate forms, try whirling in a centrifuge, or vigorous shaking. Decant the solution and add 1 ml. of alcohol (?). (SEPARATION OF K^+ FROM NA^+.)

(81) Sodium, Na^+. (*a*) *Flame Test.*—Clean a platinum wire as in (**69,** *c*) and make a flame test on a drop of dilute NaCl solution (?). Clean the wire again, draw through the fingers, and try the flame color. Compare the duration intensity in the two cases (?).

(*b*) *Sodium Zinc Uranyl Acetate.*—Dilute 1 drop of NaCl solution to about 1 ml. and add 1 or 2 drops of zinc uranyl acetate solution, $HZn(UO_2)_3(C_2H_3O_2)_9$ (?, E). The formula of the precipitate is $NaZn(UO_2)_3(C_2H_3O_2)_9$. Does this precipitate form immediately? (SEPARATION FROM K^+.)

(*c*) *Sodium Perchlorate.*—Dilute 1 or 2 drops of NaCl solution to 1 ml. and add 1 drop of $Zn(ClO_4)_2$ solution (?). (See K^+ ions.)

(82) Ammonium, NH_4^+. (*a*) *Action of Strong Bases on Ammonium Salts.*—Place 1 or 2 drops of NH_4Cl in a small beaker or casserole and add about the same volume of NaOH solution (E). Cover with a watch glass, to the lower side of which is stuck a piece of moist red litmus paper. Warm gently and note the effect (?).

Notes.—1. Several facts combine to bring about the displacement of free NH_3 from ammonium salts by strong bases. The interlocking equilibriums may be represented as follows:

$$NH_4^+ + OH^- \underset{(1)}{\rightleftarrows} NH_4OH \underset{(2)}{\rightleftarrows} \left\{\begin{array}{l} NH_3 \text{ (dissolved)} \underset{(3)}{\rightleftarrows} NH_3 \text{ (gas)} \\ H_2O \end{array}\right.$$

In the first place, NH_4OH is a very weak base, a molar solution being ionized only 0.4 per cent; hence reaction (1) proceeds to the right almost to completion. In the second place, NH_4OH is largely dissociated into NH_3 and H_2O, as represented in reaction (2). (Some authorities regard the NH_4OH form as being non-existent.) In the third place, the solubility of NH_3 in water becomes quite low at high temperatures, according to reaction (3). At high temperatures, then, reaction (3) is practically complete, and hence reactions (2) and (1) will, in turn, be made to go to practical completeness. Note that the removal of NH_3 depends wholly on reaction (3). Reactions (1) and (2) merely operate to convert NH_4^+ with practical completeness into dissolved NH_3.

✓2. Since NH_4^+ compounds have been introduced into the solution as reagents in Groups III and IV, the test for NH_4^+ must be made on a fresh sample of the unknown.

3. If the mixture is allowed to boil, enough NaOH may be carried up in the spray to give a blue color to the litmus paper.

✓4. Hg^{++} and Hg_2^{++} ions interfere with this reaction by forming amino compounds of high stability. These interfering cations, if present, should be precipitated as sulfides by H_2S before adding the NaOH reagent.

(*b*) *Interference with the Potassium Test.*—Dilute 1 drop of NH_4Cl solution to about 1 ml. and add 1 drop of $Zn(ClO_4)_2$ solution. If no precipitation occurs, increase the concentrations of NH_4^+ and ClO_4^- by adding a few more drops of NH_4Cl and

$Zn(ClO_4)_2$ to the mixture (?). Under what circumstances does NH_4^+ interfere with the ClO_4^- test for K^+?

(*c*) *Removal of Ammonium Salts.*—Place about 0.5 ml. of NH_4Cl in a small beaker, evaporate to dryness, and carefully heat the beaker just below red heat (?). Explain why the gas formed in the beaker changes to white fumes upon cooling? Note whether the salt tends to recondense (*i.e.*, sublime) on the cold sides of the beaker.

Repeat the experiment, only adding 1 ml. of concentrated HNO_3 before evaporating and moistening the residue with a drop of concentrated HNO_3 just before ignition. Does a sublimate form in this case?

Which appears to be the better method for expelling ammonium salts?

Notes.—1. Upon heating, NH_4Cl dissociates according to the equation: $NH_4Cl + \text{heat} \rightleftarrows NH_3 + HCl$. As inferred from the Le Chatelier principle, the degree of dissociation is much greater at high temperatures. As a result, a sublimate of solid NH_4Cl tends to form whenever hot vapors come in contact with a relatively colder surface and may fall back into the beaker to enter again upon a cycle of vaporization and sublimation.

2. Upon strong heating, NH_4NO_3 decomposes into water and nitrous oxide, thus: $NH_4NO_3 \rightarrow 2H_2O + N_2O$. Strictly speaking, decomposition differs from dissociation in that the former is irreversible.

Exercises

1. Formulate the equilibrium existing in a suspension of $Mg(OH)_2$ in water. How would this equilibrium be affected by the addition of an NH_4^+ salt?
2. $Mg(OH)_2$ is about as insoluble as $PbSO_4$. Why would NaOH not be a suitable reagent for its separation?
3. NH_4Cl prevents the precipitation of $Mg(OH)_2$ by NH_4OH. Would NaCl also prevent the precipitation of $Mg(OH)_2$ by NaOH? Why?
4. Upon washing with water, $MgNH_4PO_4$ tends to hydrolyze, forming $MgHPO_4$. Write the equation. How may this hydrolysis be prevented?
5. Which cation does NH_4^+ resemble, Na^+ or K^+?
6. Suggest a mercury compound that might be used instead of red litmus in the test for NH_3 vapors. How would you proceed with the test?
7. Name two precipitants for Na^+; two for K^+.
8. Why are Na^+ and K^+ usually precipitated in alcoholic solution?
9. Just how do NH_4^+ ions interfere with the tests for Na^+ and K^+?
10. $(NH_4)_2SiF_6$ is soluble in water. Explain the precipitation when NH_4OH is added to H_2SiF_6.

11. Why is the test for NH_4^+ always made on a portion of the original?
12. What is the difference between decomposition and dissociation? Illustrate by the action of heat on dry NH_4Cl and dry NH_4NO_3.
13. Which gives the stronger flame test, NaCl or Na_2SO_4? Would the test for Na^+ in Na_2SO_4 be improved by adding HCl? What would be the residue if a mixture of Na_2SO_4 and HCl was evaporated to dryness?
14. How could Mg^{++} be separated from Na^+ and K^+ without introducing Na^+ ions?
15. Name suitable reagents for the following one-step separations: (*a*) $Mg(NO_3)_2$ and KNO_3, (*b*) $MgCl_2$ and NaCl, (*c*) KNO_3 and $NaNO_3$, (*d*) $NaNO_3$ and NH_4NO_3.

ANALYSIS

(**83**) Follow *A* or *B*, according to the nature of the unknown.

A. The Unknown Contains Group V Only.—Use 2-drop portions to test for Mg^{++}, NH_4^+, K^+, and Na^+ according to (**85**) to (**89**).

B. The Unknown Is a Filtrate from Group IV.—Add 1 ml. of concentrated HNO_3 and evaporate the solution to dryness in a casserole. Ignite the residue as long as white fumes are driven off, so as to expel NH_4^+ salts. Take up the residue in 3 ml. of warm water (plus 1 drop of dilute HCl, when necessary). Transfer the solution to a test tube and make it alkaline with 2 drops of NH_4OH. Heat the solution in the water bath [see (**72**)] and add $(NH_4)_2CO_3$ dropwise until precipitation is complete. Centrifuge or filter, and reject the precipitate. Test the solution by (**85**) to (**89**).

Notes.—1. The purpose of the evaporation and ignition is the expulsion of the excess of NH_4^+ salts, which have been responsible for the incomplete precipitation of the Group IV carbonates; *e.g.*, $CaCO_3 + 2NH_4^+ \rightleftarrows Ca^{++} + (NH_4)_2CO_3$.

2. The residue insoluble in water consists of MgO, along with small amounts of the oxides of Ba^{++}, Sr^{++}, and Ca^{++}.

3. Group IV cations must be removed, since they interfere with the test for Mg^{++} by forming precipitates with the PO_4^{---} ion.

(**84**) **Flame Tests.**—Make a flame test on the solution from (**83**), using a clean platinum wire [see (**69**, *c*)]. A yellow color indicates *sodium,* and a violet color indicates *potassium.* If Na^+ is present, observe the flame through a thick (or double) cobalt glass. A purple color indicates *potassium.*

(85) Magnesium.—Proceed according to *A* or *B*.

A. The Unknown Contains Group V Only.—Dilute 2 drops of the unknown solution to 1 ml. and add 3 drops of NH_4Cl or NH_4NO_3 and 2 drops of *clear* Na_2HPO_4 solution. Then add NH_4OH drop by drop until the mixture is slightly alkaline. A white precipitate of $MgNH_4PO_4$ indicates *magnesium.*

B. The Solution Is a Filtrate from Group IV.—To a 1-ml. portion of the solution reserved from (**83,** *B*), add a few drops of *clear* Na_2HPO_4 solution and then NH_4OH drop by drop until the mixture is slightly alkaline. A white precipitate of $MgNH_4PO_4$ indicates *magnesium.*

Lake Test for Mg^{++}.—In case of doubt, the above tests for Mg^{++} may be confirmed as follows: Centrifuge or filter, and wash the precipitate with a little cold water to remove soluble NH_4^+ salts. Dissolve the precipitate in 1 ml. of water plus 1 or 2 drops of dilute HCl. Add 1 drop of *p*-nitrobenzeneazoresorcinol ("S. and O. reagent") and add dilute NaOH solution dropwise until the yellow color of the dye changes to violet. Centrifuge. A blue lake confirms the presence of *magnesium.*

(86) Ammonium.—Place 1 ml. of the original solution (or a small amount of the solid) in a crucible and add 1 ml. of NaOH solution. Cover the crucible with a small watch glass carrying on its lower side a piece of moist red litmus paper. If there is no reaction, warm gently on a triangle over a water bath. A blue color indicates the presence of *ammonium.*

(87) The Alkali Ions.—If the solution is an unknown on Group V only, use a 2-drop portion, diluted to 1 ml.; if the solution is a filtrate from Group IV or previous groups, use the remainder of the solution reserved from (**83,** *B*).

Removal of Phosphate and Oxalate.—If the solution is an unknown on Group V only, or if it is a filtrate from previous groups not containing any of the ions of the Iron subgroup, Group IV, and Mg^{++}, the anions PO_4^{---} and $C_2O_4^{--}$ may be present. In such a case, barely alkalize the solution with NH_4OH and add $Ca(C_2H_3O_2)_2$ solution drop by drop until precipitation (if any) is complete. Centrifuge or filter, and reject the precipitate. Use the solution for (**88**).

Note.—$Ca(C_2H_3O_2)_2$ removes PO_4^{---} and $C_2O_4^{--}$, which would interfere with the $HZn(UO_2)_3(C_2H_3O_2)_9$ test for Na^+ by precipitating UO_2HPO_4 and $UO_2C_2O_4$.

Removal of NH_4^+ Ions.—To the solution free from PO_4^{---} and $C_2O_4^{--}$, add 1 ml. of concentrated HNO_3 and evaporate the solution to dryness, as in (**83,** *B*). Ignite the residue until NH_4^+ is expelled. After cooling, take up the residue in 1 ml. of water and 1 or 2 drops of $HC_2H_3O_2$ and reserve for (**88**).

(**88**) **Potassium.**—To the solution from (**87**) add an equal volume of alcohol. If a precipitate forms, centrifuge or filter,

TABLE XI.—ANALYSIS OF GROUP V

<table>
<tr><td colspan="2">(83) Follow <i>A</i> or <i>B</i>, according to the nature of the unknown.</td></tr>
<tr><td><i>A</i>. Solution: Mg^{++}, NH_4^+, K^+, Na^+, and possibly PO_4^{---}, $C_2O_4^{--}$. Use 2-drop samples for the tests in (84), (85), (86), (87), (88).</td><td><i>B</i>. Filtrate from preceding groups: Mg^{++}, NH_4^+, K^+, Na^+; possibly traces of Ba^{++}, Sr^{++}, Ca^{++}; or PO_4^{---}, $C_2O_4^{--}$. Add HNO_3, evaporate, ignite. Dissolve residue in water + HCl. Add NH_4OH, $(NH_4)_2CO_3$, filter, reject precipitate. Reserve solution for (84), (85), (87), (88).</td></tr>
<tr><td colspan="2">(84, <i>A</i> and <i>B</i>) Make flame test on a portion of the solution from (83, <i>A</i> or <i>B</i>).</td></tr>
<tr><td>(85) <i>A</i>. Dilute 2 drops of solution from (83, <i>A</i>), add NH_4Cl, Na_2HPO_4, NH_4OH.
Precipitate: White $\underline{MgNH_4PO_4}$.</td><td>(85) <i>B</i>. To a portion of the solution from (83, <i>B</i>), add Na_2HPO_4, NH_4OH.
Precipitate: White $\underline{MgNH_4PO_4}$.</td></tr>
<tr><td colspan="2">(86) <i>A</i> and <i>B</i>. Solution: 2 drops of original unknown. Add NaOH, warm and test vapors with red litmus paper. Blue color indicates NH_4^+.</td></tr>
<tr><td colspan="2">(87) <i>A</i> and <i>B</i>. Besides Mg^{++}, K^+, Na^+, NH_4^+, the solution may contain PO_4^{---}, $C_2O_4^{--}$. Add NH_4OH, $Ca(C_2H_3O_2)_2$.
Precipitate: $\underline{Ca_3(PO_4)_2,\ CaC_2O_4}$. Filter, reject precipitate.
Solution: K^+, Na^+, Mg^{++}, Ca^{++}, NH_4^+. Remove NH_4^+ by adding HNO_3, evaporating, and igniting residue. Cool, take up residue in water + $HC_2H_3O_2$.</td></tr>
<tr><td colspan="2">(88) Solution: Mg^{++}, K^+, Na^+, Ca^{++}. Acidify with $HC_2H_3O_2$. Add alcohol and reject any precipitate. Add $Zn(ClO_4)_2$.
Precipitate: White $\underline{KClO_4}$. Centrifuge and reserve solution for (89).</td></tr>
<tr><td colspan="2">(89) Solution: Na^+, Mg^{++}, Ca^{++}, alcohol. Add $HZn(UO_2)_3(C_2H_3O_2)_9$.
Precipitate: White $\underline{NaZn(UO_2)_3(C_2H_3O_2)_9}$.</td></tr>
</table>

and discard the precipitate. To the clear alcoholic solution add several drops of $Zn(ClO_4)_2$ solution, mix well, and let stand a few minutes. A white precipitate indicates *potassium.* Decant or filter, and reserve solution for (**89**).

Notes.—1. NH_4^+ ions must be removed since, if present in quantity, they might interfere with the test for K^+ by precipitating slightly soluble NH_4ClO_4.

2. Sometimes the addition of alcohol causes a partial precipitation of substances slightly soluble in alcohol, *e.g.*, Na_2SO_4, KNO_3, etc. Sufficient K^+ and Na^+ are left in solution for their detection in their proper places.

3. The alcohol reduces the solubility of $KClO_4$, thereby increasing the sensitiveness of the test.

(**89**) **Sodium.**—To the solution reserved from (**88**), add 3 drops of $HZn(UO_2)_3(C_2H_3O_2)_9$ solution, with vigorous shaking. Allow to stand several minutes. A white or lemon-yellow precipitate, $NaZn(UO_2)_3(C_2H_3O_2)_9$, indicates *sodium.*

PART III

THE DETECTION OF THE ANIONS

Anion analysis differs from cation analysis very sharply in one respect, *viz.*, anion analysis depends upon the interpretation of a mass of reactions, rather than a routine of separations followed by confirmatory tests. For this reason, a careful study of the preliminary experiments on the anions is even more important than those on the cations.

Anion Groups and Group Reagents.—As a basis for classification (not *separation*), anions are divided into groups, using Ag^+, Ba^{++}, and Ca^{++} as the principal group reagents. Only the commoner anions are included:

Group I (Ag^+ salts insoluble in dilute HNO_3):

Cl^-
Br^-
I^-
CN^-
SCN^-
$Fe(CN)_6^{----}$
$Fe(CN)_6^{---}$
S^{--}
$S_2O_3^{--}$ (?)

Group II (Ag^+ salts sparingly soluble in cold water):

$C_2H_3O_2^-$
NO_2^-
OH^-

Group III (Ag^+, Ba^{++}, and Ca^{++} salts insoluble in water but soluble in dilute HNO_3):

CO_3^{--}
$C_2O_4^{--}$
SO_3^{--}
$S_2O_3^{--}$ (?)
BO_3^{---} (or BO_2^-)
PO_4^{---}
AsO_4^{---} (or AsO_3^-)
AsO_3^{---} (or AsO_2^-)
CrO_4^{--} (or $Cr_2O_7^{--}$)

Group IV (Ag^+, Ba^{++}, and Ca^{++} salts soluble in water):

NO_3^-
ClO_3^-
ClO_4^-
MnO_4^-

Group V (Ag^+ salts soluble in water, Ba^{++} and Ca^{++} salts insoluble in dilute HNO_3):

SO_4^{--}
F^-
SiF_6^{--}

Group VI (anions which form precipitates of H_2SiO_3 upon acidification and warming):

The various silicate anions, as SiO_3^{--}, SiO_4^{----}, $Si_2O_7^{------}$, etc.

GROUP I

This group contains those anions whose Ag^+ salts are insoluble in water and in dilute HNO_3, but whose Ba^{++} salts are soluble in water.

Chloride, Cl^-.
Bromide, Br^-.
Iodide, I^-.
Thiocyanate, SCN^-.

Cyanide, CN^-.
Ferrocyanide, $Fe(CN)_6^{----}$.
Ferricyanide, $Fe(CN)_6^{---}$.
Sulfide, S^{--}.

The group may be roughly divided into subgroups, as shown above, by their reactions with such cations as Co^{++}, Ni^{++}, etc. The Co^{++} halides and thiocyanate are soluble in water, while the cyanide, ferrocyanide, ferricyanide, and sulfide are insoluble.

PRELIMINARY EXPERIMENTS

Note to Instructor.—At this point, the instructor should announce to the class the anions to be included in the course and should list the preliminary experiments to be performed. Not only the preliminary experiments on the anions that are not included but also certain others may be omitted, depending on the analytical procedures to be used.

(90) Chloride, Cl^-. (*a*) *Reaction with Concentrated Sulfuric Acid.*—Evaporate 1 drop of NaCl solution to dryness in a crucible. Cool thoroughly and moisten the residue with 1 drop of concentrated H_2SO_4 (?, E). Hold a piece of moist blue litmus paper in the mouth of the crucible (?). Is there any evidence of the presence of free chlorine?

Note.—HCl differs from HBr and HI in not being oxidized by concentrated H_2SO_4.

(*b*) *Silver Chloride.*—Dilute 1 drop of NaCl solution to about 1 ml. and add 1 drop of $AgNO_3$ solution (?, E). Divide the mixture into two parts. Test the solubility of one part in HNO_3 (?) and test the other part in NH_4OH (?, E). Reserve the first part for (*c*), following.

(*c*) *Decomposition of Silver Chloride by Sodium Hydroxide.*—Drain and wash the portion of AgCl reserved from the preceding experiment and warm it with 10 per cent NaOH solution. Is there any visible effect? Dilute to about 4 ml. and filter. Acidify the filtrate with HNO_3 and add 1 drop of $AgNO_3$ (?). Represent the reaction of NaOH on AgCl by a reversible equation.

(91) Bromide, Br^-. (*a*) *Reaction with Concentrated Sulfuric Acid.*—Evaporate 1 drop of KBr solution to dryness in a crucible. Allow the crucible to cool and add 1 drop of concentrated H_2SO_4. Test the fumes evolved with a piece of moist blue litmus (?), also with a piece of starch-iodide paper (?). What substances are responsible for these reactions? Complete and balance the equations: $Br^- + H^+ \rightarrow$?; $HBr + H_2SO_4 \rightarrow Br_2 +$? + ?.

(*b*) *Silver Bromide.*—Dilute 1 drop of KBr to 1 ml. and add 1 drop of $AgNO_3$ solution (?, E). Note its color and general appearance. Divide the precipitate into two portions and try their solubilities in HNO_3 (?) and in NH_4OH (?). Reserve an AgBr residue for (*d*), below.

Note.—White and yellow cannot be distinguished by artificial (yellow) light.

(*c*) *Displacement by Chlorine.*—Dilute 1 drop of KBr solution to about 1 ml. and add Cl_2 solution dropwise (?, E). Now add several drops of CCl_4 and shake or centrifuge (?). Is this color due to the bromine molecule, Br_2, or the bromide ion, Br^-?

(*d*) *Decomposition of Silver Bromide by Sodium Hydroxide.*—Boil a portion of the AgBr precipitate reserved from (*b*) above with 1 per cent NaOH solution, filter or centrifuge, and test the filtrate for Br^- by HNO_3 and $AgNO_3$. Compare results with (**90,** *c*). Boil a second portion with 0.1 per cent NaOH solution and test filtrate for Br^- as before (?).

(92) Iodide. (*a*) *Reaction with Concentrated Sulfuric Acid.*—To a small particle of solid KI in a test tube, add 1 drop of concentrated H_2SO_4 (?). Test for HI with a rod that has been dipped in NH_4OH (?). Account for the presence of I_2, SO_2, S, and H_2S by balancing the following equations: $HI + H_2SO_4 \rightarrow SO_2$, etc.; $HI + H_2SO_4 \rightarrow S$, etc.; $HI + H_2SO_4 \rightarrow H_2S$, etc.

(*b*) *Displacement by Chlorine.*—Dilute 1 drop of KI solution to 1 ml. and add several drops of chlorine solution (?, E). Add about 0.5 ml. of CCl_4 and shake or centrifuge (?).

(*c*) *Oxidation by Nitrous Acid.*—Dilute 1 drop of KI solution to about 1 ml. and add 2 drops of $NaNO_2$ solution and 1 drop of dilute H_2SO_4 (?). Complete the equation $HI + HNO_2 \rightarrow$? + ? + ?.

Notes.—1. This reaction is useful in separating I^- from Cl^- and Br^- Neither HCl nor HBr is oxidized by HNO_2.

2. SCN^- ions are also oxidized by HNO_2, forming a red solution. The reaction is therefore useful for separating I^- but not for its identification.

(*d*) *Silver Iodide.*—Dilute 1 drop of KI solution to about 1 ml. and add 1 or 2 drops of $AgNO_3$ (?, E). Add about 0.5 ml. of NH_4OH, centrifuge, and acidify the solution with HNO_3. Is AgI soluble in NH_4OH?

(*e*) *Reducing Action.*—Dilute 1 drop of KI solution to about 1 ml. and acidify with 1 drop of dilute HCl. Now add 1 drop of $FeCl_3$ and note the red color produced (?, E). I^- in acid solution is a strong reducing agent.

(**93**) **Cyanide, CN^-.**[1] (*a*) *Reaction with Acids.*—Cyanides react with acids, forming hydrocyanic ("Prussic") acid, HCN, a deadly poisonous gas.

(*b*) *Formation of Ferrocyanide and Prussian Blue.*—Dilute 2 drops of sodium cyanide and add 1 or 2 drops of ferrous sulfate solution, $FeSO_4$, and then 1 drop of NaOH to make the mixture alkaline. Boil, and acidify with dilute HCl. A blue precipitate will probably form, owing to the fact that $FeSO_4$ usually contains Fe^{+++}. Add 1 drop of $FeCl_3$ solution (?). The blue precipitate is ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, and is called "Prussian blue." The following equations summarize the action: $6CN^- + Fe^{++} \rightarrow Fe(CN)_6^{----}$; $3Fe(CN)_6^{----} + 4Fe^{+++} \rightarrow Fe_4[Fe(CN)_6]_3$.

(**94**) **Thiocyanate, SCN^-.** (*a*) *Decomposition by Concentrated Sulfuric Acid.*—To 1 or 2 drops of NH_4SCN solution, add 1 drop of concentrated H_2SO_4 (?). No equation can be written.

(*b*) *Silver Thiocyanate.*—Dilute 1 drop of NH_4SCN solution and add 1 or 2 drops of $AgNO_3$ solution (?, E). Filter (or centrifuge) and reject the filtrate. Try the solubility of the precipitate in HNO_3 and in NH_4OH, as in (**90**, *b*) (E's).

(*c*) *Ferric Thiocyanate.*—Dilute 1 drop of NH_4SCN and add 1 drop of $FeCl_3$ (?, E). The formula for the red product is $Fe(SCN)_6^{---}$. The parent molecule may be considered $Fe_2(SCN)_6$. Divide the mixture into two portions. Shake one portion with 0.5 ml. of ether (?), and the other with 0.5 ml. of CCl_4 (?). How could you distinguish between $Fe_2(SCN)_6$ and free I_2?

---

[1] Cyanides are violent poisons, and experiments with them should be done under the oversight of an instructor. It is suggested that cyanides be omitted from elementary courses.

Notes.—1. Nitrates give a red color with SCN^- in acid solution, due to decomposition products. The red colors are displaced by boiling.

2. Certain organic anions (*e.g.*, acetate) give a red color with Fe^{+++} ions in neutral solutions, but, unlike thiocyanate, the color disappears on acidifying with HCl.

3. Iodide ions interfere, since they are oxidized by Fe^{+++} to free I_2 (brown). They must therefore be previously removed by excess Cl_2 and boiling.

(95) Ferrocyanide, $Fe(CN)_6^{----}$. (*a*) *Reaction with Concentrated Sulfuric Acid.*—The ferrocyanide ion reacts slowly with acids in the cold, forming a bluish-green solution and evolving gaseous HCN. Upon heating with concentrated H_2SO_4, CO is evolved. Equation: $Fe(CN)_6^{----} + 12H^+ + 6H_2O \rightarrow Fe^{++} + 6NH_4^+ + 6CO$.

(*b*) *Silver Ferrocyanide.*—Dilute 1 drop of $K_4Fe(CN)_6$ solution to about 1 ml. and add 1 or 2 drops of $AgNO_3$ (?, E). Divide the precipitate into two parts and try the solubilities in NH_4OH and in HNO_3 (?).

(*c*) *Prussian Blue.*—Dilute 1 drop of $K_4Fe(CN)_6$ solution and add 1 drop of $FeCl_3$ solution (?, E). [See (**93,** *b*).] Is the precipitate soluble in HCl?

(96) Ferricyanide, $Fe(CN)_6^{---}$. (*a*) *Reaction with Concentrated Sulfuric Acid.*—The ferricyanide ion is very slowly decomposed by cold, dilute acids, forming a brownish solution. Upon heating with concentrated H_2SO_4, CO is evolved: $Fe(CN)_6^{---} + 12H^+ + 6H_2O \rightarrow Fe^{+++} + 6NH_4^+ + 6CO$. See $Fe(CN)_6^{----}$

(*b*) *Silver Ferricyanide.*—Dilute 1 drop of $K_3Fe(CN)_6$ solution and add 1 or 2 drops of $AgNO_3$ (?, E). Divide into two portions and try the solubility of one portion in NH_4OH (E) and the other in dilute HNO_3 (?).

(*c*) *Reaction with Ferrous Ions.*—Dilute 1 drop of $K_3Fe(CN)_6$ and add 1 or 2 drops of $FeSO_4$ solution (?, E). Consider the precipitate to be $Fe_3[Fe(CN)_6]_2$. What is the trade name for this precipitate? Is it soluble in dilute HCl? [See (**51,** *f*).]

(*d*) *Oxidizing Action.*—Dilute 1 drop of $K_3Fe(CN)_6$ and add 1 drop of KI solution and acidify with 1 drop of dilute H_2SO_4 (?). Now add 1 drop of $FeCl_3$ (?). Complete and balance: $Fe(CN)_6^{---} + I^- \rightarrow$?; $Fe(CN)_6^{----} + Fe^{+++} \rightarrow$?.

Note.—The $Fe(CN)_6^{---}$ ion in acid solution is a strong oxidizing reagent and is reduced by many agents, such as HI, H_2S, H_2SO_3, etc. A combination of $K_3Fe(CN)_6$ and $FeCl_3$ is used in this book to detect reducing agents in anion analysis.

(97) Sulfide, S^{--}. (*a*) *Reaction with Concentrated Sulfuric Acid.*—Place 1 drop of Na_2S solution in a test tube and add 1 drop of concentrated H_2SO_4. Carefully smell the gases evolved and try to identify, by their odors, two substances present in the fumes (?). What is the primary reaction between S^{--} and H^+? Explain by means of a second equation the formation of S and SO_2 (E).

(*b*) *Silver Sulfide.*—Dilute 1 drop of $AgNO_3$ solution to 1 ml. and saturate the solution with H_2S (?, E). Centrifuge and divide the precipitate into two parts. Try the solubility of one part in cold dilute HNO_3 (?) and then in warm concentrated HNO_3 (?, E). Try the solubility of the other part in NH_4OH (?).

Note.—The separation of impure sulfur when many substances, particularly ores, are treated with HNO_3 is strongly indicative of the presence of sulfides.

(*c*) *Lead Sulfide.*—Moisten a piece of filter paper with 1 drop of $Pb(C_2H_3O_2)_2$ solution and allow H_2S to come into contact with it (?, E).

(*d*) *Solution of Insoluble Sulfides.*—Place a pinch of powdered pyrites, FeS_2, in a crucible and add a little water and 2 or 3 drops of dilute HCl. Cover the crucible with a piece of filter paper moistened with a drop of $Pb(C_2H_3O_2)_2$ solution (?). Now add a little zinc dust, mix with a stirring rod, and recover with the filter paper (?, E).

Note.—SCN^-, SO_3^{--}, and $S_2O_3^{--}$ ions are also reduced to H_2S by means of Zn + HCl.

Exercises

1. Give the colors conferred on CCl_4 by the free halogens.
2. Could an acid solution containing I^- also contain NO_2^-? Why?
3. Suggest another silver salt besides AgCl which would be decomposed by heating with NaOH solution. What is the determining factor in such cases?
4. What substances besides Fe^{+++} give a red color with SCN^-? What substances besides SCN^- give a red color with Fe^{+++}?
5. An unknown substance reacts with HNO_3, leaving a yellow, gummy residue which tends to float in the hot acid solution. Interpret.

6. What is the test for Cl^- in the absence of Br^- and I^-? What other anion of Group I interferes with this test?
7. How could AgCl be separated from a mixture of Ag_2S and AgCl?
8. Name an oxidizing agent that will oxidize HI but not HBr or HCl.
9. How would you test for S^{--} in HgS?
10. NaCN solution is slowly mixed with $AgNO_3$. Explain the two steps by ionic equations. What would be the reaction if the solutions were mixed in reverse order?
11. Describe the Prussian blue test for CN^-.
12. Draw up a table showing the colors of the Ag^+ salts of Group I.
13. Compare Br^- with Br_2 in several respects, *e.g.*, color, solubility in solvents, oxidizing action, etc.
14. What ions are present in a solution of AgCl in NH_4OH? in $Na_2S_2O_3$? in NaCN?
15. Compare the reducing power of HCl, HBr, and HI by noting their reactions on concentrated H_2SO_4.
16. Name an anion, other than SCN^-, that gives a red color with Fe^{+++}.
17. What mixture is used for a general test reagent for oxidizing agents?

GROUP II

This group contains the anions whose Ag^+ salts are sparingly soluble in cold water but readily soluble in dilute HNO_3, and whose Ba^{++} salts are soluble in water.

Nitrite, NO_2^-.
Acetate, $C_2H_3O_2^-$.
Hydroxyl, OH^-.

In practice, it is well to consider this group as a subdivision of Group IV. This follows from the lack of differentiation between dilute solutions of these anions and solutions of Group IV.

PRELIMINARY EXPERIMENTS

(98) Nitrite, NO_2^-. (*a*) *Reaction with Acids.*—Place 1 or 2 drops of $NaNO_2$ solution in a test tube and acidify with dilute H_2SO_4 (?, E). Explain (1) the blue color in the cold solution, and (2) the brown color in the gases evolved.

(*b*) *Oxidizing and Reducing Action.*—In its reaction with HI, what kind of agent is HNO_2? [See (**92**, *c*)].

Dilute 1 drop of $NaNO_2$ solution and add 1 drop each of $FeCl_3$ and $K_3Fe(CN)_6$ solutions (?). What kind of agent is HNO_2 in this case?

(*c*) *Reaction of* NO *with Ferrous Sulfate Solution.*—Place 1 drop of $NaNO_2$ solution in a test tube and add 1 drop of $FeSO_4$ solution (?). The color may be assumed to be due to $FeSO_4.NO$. Assuming the $FeSO_4$ solution to contain some free H_2SO_4, complete the following equations: $NO_2^- + H^+ \rightarrow$? $HNO_2 + Fe^{++} + H^+ \rightarrow Fe^{+++} + NO + H_2O$; $FeSO_4 + NO \rightarrow$?

(99) Acetate, $C_2H_3O_2^-$. (*a*) *Reaction with Acids.*—Place a bit of solid $NaC_2H_3O_2$ in a test tube and moisten it with concentrated H_2SO_4 (?, E). Note the vinegar-like odor.

(*b*) *Formation of Ethyl Acetate.*—Place 1 drop of $NaC_2H_3O_2$ solution in a test tube and add 1 drop each of ethyl alcohol and concentrated H_2SO_4. Note the odor. Gentle heating may be required. Complete the equation: $C_2H_5OH + HC_2H_3O_2 \rightarrow$? + ? What is the function of the concentrated H_2SO_4 in this reaction?

Note.—Ethyl alcohol in the presence of concentrated H_2SO_4 forms many other esters in a similar way, and some of them resemble $C_2H_5C_2H_3O_2$ rather closely in odor, *e.g.*, C_2H_5Br, $C_2H_5NO_2$.

(100) Hydroxide, OH^-. (*a*) *Tests for the Hydroxyl Ion.*—Besides litmus, name two other reagents for the OH^- ion and describe their reactions.

(*b*) *Hydrolytic Effects.*—Dissolve a little Na_2CO_3 in water and test for the presence of the OH^- ion with one of the reagents suggested in (*a*). What is the source of the ion? Complete the equation $CO_3^{--} + HOH \rightarrow$? + ? Does the presence of OH^- in an unknown solution necessarily indicate that the material actually contains a hydroxide or oxide?

Exercises

1. What is the effect of Na_2CO_3 on litmus and phenolphthalein? Explain.
2. How could you distinguish between dry CaO and dry $Ca(OH)_2$?
3. All nitrites contain NO_3^- as an impurity. Explain.
4. Write an equation for a reaction in which (*a*) HNO_2 acts as an oxidizing agent, and in which (*b*) HNO_2 acts as a reducing agent.
5. Strictly speaking, do you test for NO_2^- or NO in the ferrous sulfate test for NO_2^-?
6. Is the oxidation of I^- to I_2 a specific test for NO_2^-; *i.e.*, will any other ion give the same reaction?
7. Describe and explain the reaction of NO_2^- with an acidified mixture of KI and starch.

8. Name some anions that will interfere with the evolution-of-$HC_2H_3O_2$ test for $C_2H_3O_2^-$.
9. Name an anion that may give a dangerous explosion with alcohol-H_2SO_4 mixture. Would it be reasonable to assume the presence of $C_2H_3O_2^-$ in a solution containing this ion?

GROUP III

This group contains the anions whose Ag^+ and Ba^{++} salts are insoluble in water but soluble in dilute HNO_3. The colors of the Ag^+ salts are very important in the identification of the ions of this group, and for this reason the group is subdivided on the basis of whether the Ag^+ salt is white or colored.

IIIA (Ag^+ SALTS WHITE)	IIIB (Ag^+ SALTS COLORED)
Carbonate, CO_3^{--}	Phosphate, PO_4^{---}
Oxalate, $C_2O_4^{--}$	Arsenate, AsO_4^{---} (or AsO_3^-)
Sulfite, SO_3^{--}	Arsenite, AsO_3^{---} (or AsO_2^-)
Thiosulfate, $S_2O_3^{--}$	Chromate, CrO_4^{--}
Borate, BO_3^{---} (or BO_2^-)	Dichromate, $Cr_2O_7^{--}$

PRELIMINARY EXPERIMENTS

(101) Sulfite, SO_3^{--}. (*a*) *Reaction with Acids.*—Dissolve a pinch of sodium sulfite, Na_2SO_3, in 1 ml. of cold water and acidify with 1 drop of dilute HCl (E). Cautiously try the odor of the mixture (?). Save the cold solution for the next experiment.

(*b*) *Reducing Action of Sulfurous Acid.*—Dilute 1 drop of $KMnO_4$ solution to 2 ml. and add this solution dropwise to the solution reserved from (*a*) (?, E). To the colorless solution add 1 drop each of dilute HNO_3 and $Ba(NO_3)_2$ solutions (?). Ba^{++} ions in the presence of H^+ are a test for what anion? Complete the following equation: $SO_3^{--} + MnO_4^- + H^+ \rightarrow ? + ? + ?$

(*c*) *Silver Sulfite.*—Dissolve a pinch of solid Na_2SO_3 in about 1 ml. of water. Place 1 drop of this solution in a test tube and add 1 drop of $AgNO_3$ solution and a few drops of water (?, E). Boil the mixture (?). Explain by balancing the following equation: $Ag_2SO_3 \rightarrow Ag + Ag_2SO_4 + SO_2$. [See $Ag_2S_2O_3$ (**102,** *b*).] Reserve the remainder of the solution for (*d*) and (*e*).

(*d*) *Sulfate in Sulfites.*—Dilute 1 drop of the Na_2SO_3 solution reserved from (*c*) and add 1 drop of $Ba(NO_3)_2$ or $BaCl_2$. Now add 1 drop of HNO_3 or HCl. Most of the precipitate should dissolve.

The insoluble residue is $BaSO_4$. Sulfate is generally an impurity in sulfite, particularly sulfite solutions.

(*e*) *Barium, Strontium, and Calcium Sulfites.*—Dilute 1 drop of the Na_2SO_3 solution reserved from (*c*) to about 1 ml. and add 1 drop of a solution containing Ba^{++}, Sr^{++}, or Ca^{++} ions (?, E). What would happen if this mixture were saturated with gaseous SO_2?

Note.—$SrSO_3$ precipitates tend to form slowly. The reaction mixture should stand at least 1 hr. for precipitation to be complete.

(102) **Thiosulfate, $S_2O_3^{--}$.** (*a*) *Reaction with Acids.*—Dilute 1 drop of $Na_2S_2O_3$ solution and acidify with 1 drop of dilute HCl. Let the mixture stand for several minutes (?). Note the odor and precipitate and complete the equation: $S_2O_3^{--} + 2H^+ \rightarrow ? + ? + ?$.

(*b*) *Silver Thiosulfate and the Silver-Thiosulfate Complex Ion.*—Dilute 2 drops of $AgNO_3$ solution and add 1 drop of $Na_2S_2O_3$ solution (?, E). What is the color of the precipitate just after its formation? Divide the mixture into two portions. Heat the first portion (?). Complete the equation: $Ag_2S_2O_3 + ? \rightarrow Ag_2S + ? + ?$. To the second portion, add $Na_2S_2O_3$ dropwise until the reaction is complete (?). Complete and balance: $Ag_2S_2O_3 + S_2O_3^{--}$ (excess) $\rightarrow$?.

Prepare a little AgCl by diluting 1 drop of $AgNO_3$ and adding 1 drop of NaCl. Shake and pour off the liquid. Now add $Na_2S_2O_3$ solution and shake well (?, E). What would happen if this solution was acidified with HNO_3 and warmed? Try it (E).

Notes.—1. Silver thiosulfate undergoes hydrolysis, particularly upon heating, according to the equation: $Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + 2H^+ + SO_4^{--}$.

2. Various formulas have been assigned to the silver-thiosulfate complex ion. For the sake of simplicity it is written $AgS_2O_3^-$.

(*c*) *Reducing Action.*—Mix 1 drop of $FeCl_3$ with 1 drop of $K_3Fe(CN)_6$ and dilute to about 1 ml. Now introduce 1 drop of $Na_2S_2O_3$ solution (?).

Note.—Strong oxidizing agents oxidize $S_2O_3^{--}$ to SO_4^{--}: $S_2O_3^{--} + 4O + H_2O \rightarrow 2SO_4^{--} + 2H^+$. Weak oxidizing agents (*e.g.*, I_2 and Fe^{+++}) oxidize it to tetrathionate: $2S_2O_3^{--} + O + 2H^+ \rightarrow S_4O_6^{--} + H_2O$.

(103) **Carbonate, CO_3^{--}.** (*a*) *Reaction with Acids.*—Place a pinch of a solid carbonate (*e.g.*, Na_2CO_3, $CaCO_3$, etc.) in a small

flask and add a few drops of water and 1 drop of dilute H_2SO_4 (?, E).

(*b*) *Detection of CO_2.*—Dip a piece of glass tubing in $Ca(OH)_2$ solution and hold it in the gas evolved in the previous experiment (?). What is the white film that forms on the drop? Explain its disappearance in the presence of excess CO_2 (E).

Note.—Glass tubing holds a drop of solution better than a stirring rod.

The above form of the test is not sensitive and frequently fails with mineral carbonates that dissolve slowly in strong acids, *e.g.*, dolomite, $CaCO_3.MgCO_3$. In such cases a procedure such as the following is required:

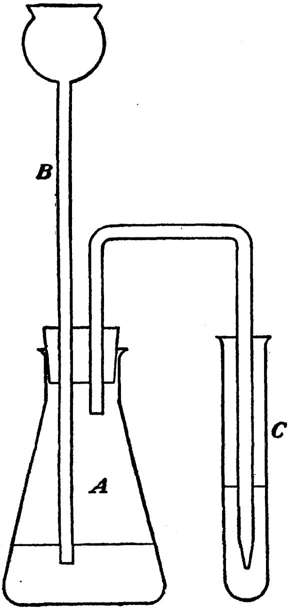

Fig. 13.—Apparatus for detecting CO_2 (macro scale).

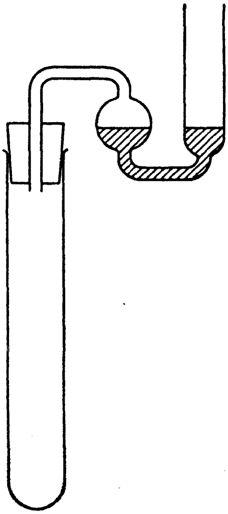

Fig. 14.—Trap for absorbing CO_2.

Place the substance in a test tube or small flask, fitted with a stopper carrying a thistle tube and a delivery tube (Fig. 13). The stem of the thistle tube should reach almost to the bottom of the tube. Introduce water until the end of the thistle tube is covered and then add dilute H_2SO_4. Bubble the gas evolved through about 1 ml. of $Ca(OH)_2$ solution in a test tube. Gentle heating in the water bath will favor the liberation of the CO_2. The introduction of a small piece of metallic zinc aids the action by forming H_2, which helps to sweep out the CO_2 gas.

A further improvement is the use of the absorption trap shown in Fig. 14.

(*c*) *Silver Carbonate.*—Dilute 1 drop of $AgNO_3$ solution and add 1 drop of Na_2CO_3 solution (?, E). This precipitate turns yellow to brown upon boiling the mixture or upon exposure to sunlight. Suggest an explanation (?).

(*d*) *Barium Carbonate.*—Write the equation for the reaction between Ba^{++} and CO_3^{--} ions (E). Describe the solubility of the product.

(104) Oxalate, $C_2O_4^{--}$. (*a*) *Reactions with Sulfuric Acid.*—Place 2 or 3 drops of $(NH_4)_2C_2O_4$ solution in a test tube, add 1 ml. of dilute H_2SO_4, and warm (?). (SEPARATION OF CO_3^{--} FROM $C_2O_4^{--}$.)

Place a pinch of solid $H_2C_2O_4$ in a small test tube and add 1 ml. of concentrated H_2SO_4. If necessary, heat carefully to start the reaction (?). Ignite the escaping gas and note the color of the flame. Complete the equation: $H_2C_2O_4$ + heat + dehydrating agent $\rightarrow$? + ? + ?.

(*b*) *Oxidation by Permanganic Acid.*—To 2 drops of $(NH_4)_2C_2O_4$ solution in a test tube, add 1 drop of dilute H_2SO_4 and 1 or 2 drops of very dilute $KMnO_4$. Warm gently to start the reaction. Test the gas evolved for CO_2 (?). Complete the equation: $C_2O_4^{--} + MnO_4^{-} + H^{+} \rightarrow ? + ? + ?$.

(*c*) *Calcium Oxalate.*—Dilute 1 drop of $CaCl_2$ solution, and add 1 drop of $(NH_4)_2C_2O_4$ (?, E). Filter or centrifuge, discard the solution, and try the solubility of the precipitate in dilute $HC_2H_3O_2$ (?).

(105) Borate, BO_3^{---} or BO_2^{-}. (*a*) *Silver Borate.*—To 2 or 3 drops of borax solution, $Na_2B_4O_7$, add 1 drop of $AgNO_3$ (?, E). The formula of the precipitate is written $AgBO_2$.

(*b*) *Calcium Borate.*—Dilute 1 drop of $Na_2B_4O_7$ solution and add 1 drop of $Ca(NO_3)_2$ solution (?, E). Consider the precipitate to be the metaborate, $Ca(BO_2)_2$. Divide the mixture into two parts. To one part add HNO_3 (?), and to the other, NH_4Cl solution, warming if necessary (?).

(*c*) *The Turmeric Reaction.*—Place 1 drop of $Na_2B_4O_7$ (borax) solution on a piece of turmeric paper, add 1 drop of dilute HCl, and dry the paper on a watch glass over a beaker of boiling water. What is the color of the dried spot? Touch the spot with 1 drop of dilute NaOH solution (?).

Note.—Free H_2SO_4 interferes with this test by charring the paper on concentration. It must previously be removed, *e.g.*, by precipitation by $BaCl_2$.

(*d*) *The Flame Test.*—Put a little powdered borax in a crucible, add 2 drops of concentrated H_2SO_4, a few drops of ethyl alcohol, and about 2 grams of clean sand. Mix well with a stirring rod. Warm the crucible on a wire gauze and set fire to the vapor (?). The color of the flame is due to the burning of ethyl borate, $(C_2H_5)_3BO_3$. Write equations for its preparation from the materials used.

Note.—The sand acts as a wick and assists in vaporizing the inflammable liquids.

(106) Phosphate, PO_4^{---}. (*a*) *Silver Phosphate.*—Dilute 1 drop Na_2HPO_4 to about 1 ml. and add 1 drop of $AgNO_3$ solution (?, E). Note the color of the precipitate. It is readily soluble in dilute HNO_3 and in NH_4OH.

(*b*) *Barium Phosphate.*—Dilute 1 drop of Na_2HPO_4 to about 1 ml. and add 1 drop of $Ba(NO_3)_2$ (?, E). The precipitate is soluble in $HC_2H_3O_2$.

(*c*) *Reaction with Molybdate Mixture.*—Dilute 1 or 2 drops of Na_2HPO_4 solution and add 3 or 4 drops of $(NH_4)_2MoO_4$-HNO_3 mixture. Warm in a water both for several minutes (?). Complete and balance the equation: $PO_4^{---} + NH_4^+ + H^+ + MoO_4^{--} \rightarrow (NH_4)_3PO_4.12MoO_3 + ?$.

(107) Arsenite, AsO_3^{---}, and Arsenate, AsO_4^{---}. (*a*) *Colors of Silver Arsenite and Silver Arsenate.*—Dilute 1 drop of Na_3AsO_3 solution to about 1 ml., and add 1 drop of $AgNO_3$ solution (?, E). Repeat the experiment, using K_3AsO_4 instead of Na_3AsO_3 (?, E). Both precipitates are soluble in NH_4OH and in dilute HNO_3.

(*b*) *Barium Arsenite and Barium Arsenate.*—Write equations for preparing $Ba_3(AsO_3)_2$ and $Ba_3(AsO_4)_2$. Are they soluble in HNO_3 and in HCl?

(*c*) *Reaction of Arsenate with Molybdate Mixture.*—Dilute 1 or 2 drops of Na_3AsO_4 and add 3 or 4 drops of $(NH_4)_2MoO_4$-

HNO_3 mixture (the reagent for PO_4^{---}) and warm in a water bath (?). The formula for the precipitate is considered to be $(NH_4)_3AsO_4.12MoO_3$.

Arsenite, AsO_3^{---}, gives the same reaction, owing to oxidation of AsO_3^{---} to AsO_4^{---} by the excess of HNO_3 in the molybdate reagent.

(*d*) *Separation of Arsenate from Phosphate.*—Recall that As_2S_{3-5} can be precipitated from AsO_4^{---} by means of H_2S. High acidity and high temperature favor the precipitation. Iodide must *not* be added, since I^- ions reduce the MoO_4^{--}, forming a blue sol ("molybdenum blue"). Probably the best way to separate AsO_4^{---} from PO_4^{---} is to evaporate the solution to dryness, take up the residue in concentrated HCl, and saturate the hot solution with H_2S. It should be remembered that As_2S_{3-5} separates slowly.

(**108**) **Chromate, CrO_4^{--}, and Dichromate, $Cr_2O_7^{--}$.** (*a*) *Silver Chromate.*—Dilute 1 drop of K_2CrO_4 solution to about 1 ml. and add 1 drop of $AgNO_3$ solution (?, E). Note the color of the precipitate (?). Is it soluble in HNO_3? in NH_4OH?

(*b*) *Barium Chromate.*—Recall the preparation (E) and the solubility (?) of $BaCrO_4$. [See (**69,** *b*).]

(*c*) *Equilibrium between CrO_4^{--} and $Cr_2O_7^{--}$.*—Complete the equilibrium: $CrO_4^{--} + ? \rightleftarrows Cr_2O_7^{--} + ?$ Indicate colors of these anions.

Note.—The equilibrium may not be so simple as here represented. It is probable that $HCrO_4^-$ is an intermediate in the system.

(*d*) *Oxidizing Action.*—Recall the action of H_2S on an acidified solution of $K_2Cr_2O_7$. [See (**48,** *f*).]

To a little $MnCl_2$-HCl mixture add 1 drop of $K_2Cr_2O_7$ solution (?).

(*e*) *The Hydrogen Peroxide Reaction.*—Recall the action of H_2O_2 on acidified solutions of chromates (and dichromates) in the presence of ether. [See (**48,** *d*).]

Exercises

1. In the test for CO_3^{--} in an unknown, a white precipitate formed in the limewater but later dissolved. Was a carbonate present?
2. What anion other than CO_3^{--} sometimes gives, upon acidification with dilute H_2SO_4, a positive limewater test?

3. Give an easy way for removing $CaCO_3$ from a $CaCO_3$-CaC_2O_4 mixture.
4. How could SO_2 be removed from a mixture of CO_2 and SO_2?
5. How could an arsenate be distinguished from a phosphate?
6. Why should the presence of free H_2SO_4 vitiate the turmeric test for BO_3^{---}?
7. Give quick methods for distinguishing between (*a*) Na_2CO_3 and Na_2SO_3, (*b*) Na_2SO_3 and $Na_2S_2O_3$, (*c*) K_3AsO_3 and K_3AsO_4.
8. How would you test for CO_3^{--} in an unknown containing SO_3^{--} or $S_2O_3^{--}$?
9. Suggest a solution that may be used as a substitute for limewater in the test for CO_2.
10. Write equations for the successive reactions of CO_2 with $Ca(OH)_2$.
11. Write an equation for the reaction that results when a solution of H_2SO_3 is saturated with H_2S.
12. How would you test for SO_3^{--} in the presence of $S_2O_3^{--}$?
13. Write equations for the reactions of SO_3^{--} with (*a*) $MnO_4^- + H^+$, (*b*) H_2O_2, (*c*) concentrated HNO_3.
14. Describe the following reactions: (*a*) 1 drop of $Na_2S_2O_3$ solution is added to a solution of $AgNO_3$; (*b*) 1 drop of $AgNO_3$ solution is added to a solution of $Na_2S_2O_3$. Explain the difference.
15. What cation is most suitable for the separation of SO_3^{--} and $S_2O_3^{--}$?
16. How would you distinguish between CrO_4^{--} and $C_2O_7^{--}$?
17. What is the best procedure for separating AsO_4^{---} from PO_4^{---}?
18. Write equation to illustrate the reducing action of $H_2C_2O_4$.
19. What members of anion Group III are (*a*) reducing agents, (*b*) oxidizing agents?
20. How could you distinguish between $MgNH_4PO_4$ and $MgNH_4AsO_4$ by means of $AgNO_3$?
21. All the anions of Group I interfere with the confirmation of AsO_4^{---} in $MgNH_4AsO_4$ by $AgNO_3$. Explain.

GROUP IV

This group contains those anions whose Ag^+, Ba^{++} and Ca^{++} salts are soluble in water.

Nitrate, NO_3^-.
Chlorate, ClO_3^-.
Perchlorate, ClO_4^-.
Permanganate, MnO_4^-.

On account of the appreciable solubility of $AgNO_2$ and $AgC_2H_3O_2$ in water, NO_2^- and $C_2H_3O_2^-$ ions (Anion Group II) may, in practice, be considered as belonging to this group.

PRELIMINARY EXPERIMENTS

(109) Nitrate. (*a*) *Stability of Nitric Acid.*—Place a bit of solid $NaNO_3$ in a test tube and add 1 drop of concentrated H_2SO_4. If necessary, warm gently to bring about the reaction (?, E). Look down through the tube for evidence of brown fumes. Compare the stability of HNO_3 with that of HNO_2. [See (**98,** *a*).]

(*b*) *Reduction by Ferrous Sulfate.*—Mix 1 drop of $NaNO_3$ solution with 1 drop of $FeSO_4$ solution and dilute with a few drops of water. By means of a pipette, introduce near the bottom of the tube several drops of concentrated H_2SO_4, so as to form two layers. Let the tube stand about 1 min. Recall (**98,** *c*) and account for the reaction. Complete the equations:

$$NO_3^- + H^+ \rightarrow ?$$
$$Fe^{++} + HNO_3 + H^+ \rightarrow Fe^{+++} + ? + ?$$
$$FeSO_4 + ? \rightarrow ?$$

Explain why the color forms at the junction of the two layers and not throughout the $FeSO_4$ solution (?). This reaction is the basis for the "brown-ring" test for NO_3^-. Suggest some ions (cations and anions) that would be expected to interfere.

(*c*) *Reduction of NO_3^- to NH_3 by Zinc.*—Place 1 or 2 drops of $NaNO_3$ solution in a crucible and add a pinch of zinc dust and about 0.5 ml. of concentrated NaOH solution. Cover the crucible with a watch glass carrying on its lower side a piece of moistened red litmus paper. Warm, but *do not boil* (?). Complete the equation:

$$NO_3^- + Zn + OH^- + ? \rightarrow NH_3 + HZnO_2^-$$

Note.—NH_4^+ and NO_2^- interfere with this test, both evolving NH_3. The NH_4^+ may be removed by warming with NaOH before adding the zinc. There is no easy way to separate NO_2^- from NO_3^-. However, nitrites always contain nitrates as an impurity, so that the presence of NO_3^- may be assumed whenever NO_2^- is present.

(110) Chlorate. (*a*) *Chloric Acid.*—Place a very small crystal of $KClO_3$ on a watch glass and introduce 1 drop of concentrated H_2SO_4 on its side. Bring the crystal into contact with the H_2SO_4 by means of a glass fiber and note the color of the solution

(?). This color seems to be due to a solution of ClO_2 in H_2SO_4. Balance the equation:

$$HClO_3 \rightarrow HClO_4 + ClO_2 + H_2O$$

Name some ions that would interfere with this test for ClO_3^-.

Note.—$HClO_3$ is exceedingly unstable and decomposes (sometimes with violence), forming perchloric acid, chlorine dioxide, and water. Chlorine dioxide is a yellow-green gas and dissolves in concentrated H_2SO_4, giving a yellow solution.

(*b*) *Silver Chlorate.*—Dilute 1 drop of $KClO_3$ solution to 1 ml. and add 1 drop of $AgNO_3$ solution (?).

(*c*) *Reduction of Chlorate to Chloride by Zinc.*—Place 1 drop of $KClO_3$ solution in a test tube, add a pinch of zinc dust, and acidify with dilute H_2SO_4. When the reaction is complete, centrifuge or filter, and add $AgNO_3$ to the decantate (?). Complete the equation:

$$ClO_3^- + Zn + H^+ \rightarrow ? + ? + ?$$

Note.—A similar reduction takes place in alkaline medium, when NaOH is used instead of H_2SO_4. In this case the filtrate should be acidified with HNO_3 before adding the $AgNO_3$.

(111) Perchlorate. (*a*) *Stability of Perchloric Acid.*—Warm a drop of perchloric acid, $HClO_4$, in a test tube in a water bath. Note the lack of odor. Is $HClO_4$ stable? (See $HClO_3$.)

Try to reduce $HClO_4$ to Cl^- by means of zinc plus dilute H_2SO_4 (?). [See (**110**, *c*).]

(*b*) *Decomposition of Perchlorates by Ignition.*—Place a drop of $HClO_4$ in a small casserole and neutralize it with Na_2CO_3. Add a drop of 50 per cent $Mn(NO_3)_2$ solution, evaporate to dryness, and ignite until the whole residue is blackened. Complete the equations:

$$Mn(NO_3)_2 \ (+ \text{heat}) \rightarrow MnO_2 + ?$$
$$NaClO_4 \ (+ MnO_2) \ (+ \text{heat}) \rightarrow NaCl + ?$$

Extract the residue with a little warm water and test the extract for Cl^-. Devise a procedure to detect Cl^-, ClO_3^-, and ClO_4^- in the presence of all of them.

Notes.—1. It will be remembered that MnO_2 catalyzes the decomposition of perchlorates (and chlorates) by heat.

2. The reaction must be carried out in alkaline medium. In acid medium, HCl would be formed, and the MnO_2 would oxidize it to Cl_2, which would be lost.

(112) Permanganate.—Recall the behavior of MnO_4^- ions in cation analysis and write equations for the following reactions: (1) reduction by H_2S in Group II, (2) precipitation of MnS, (3) oxidation of Mn^{++} to MnO_2, and (4) oxidation of MnO_2 to $HMnO_4$. Indicate the colors of the Mn compounds involved.

Exercises

1. How can water solutions of chromates be distinguished from dichromates by means of litmus paper?
2. List the anions that could be present in an acidified solution containing MnO_4^-.
3. How could KNO_2 and KNO_3 be distinguished by means of the $FeSO_4$ test?
4. What ions interfere with the brown-ring test for NO_3^-?
5. How would you test for NO_3^- in the presence of (*a*) CrO_4^{--}, (*b*) $Fe(CN)_6^{---}$?
6. Can it truly be said that Ag^+ and Ba^{++} are reagents for anion Group IV?
7. How does the $FeSO_4$ test for NO_3^- differ in appearance from the $FeSO_4$ test for NO_2^-?
8. How would you separate (*a*) NH_4^+ from NO_3^-? (*b*) ClO_3^- from ClO_4^-? (*c*) MnO_4^- from ClO_4^-?
9. Which is the stronger oxidizing agent, $HClO_3$ or $HClO_4$? Cite evidence to support your opinion.
10. What are the reduction products of MnO_4^- in (*a*) acid and (*b*) alkaline solution?

GROUP V

This group contains the anions whose Ag^+ salts are soluble in water, and whose Ba^{++} or Ca^{++} salts are insoluble in water and in dilute HNO_3.

Sulfate, SO_4^{--}.
Fluoride, F^-.
Fluosilicate, SiF_6^{--}.

PRELIMINARY EXPERIMENTS

(113) Fluoride, F^-. (*a*) *Precipitation of Calcium Fluoride.*—Dilute 1 drop of NaF solution with several drops of water and add 1 drop of $CaCl_2$ or $Ca(NO_3)_2$ solution (?, E). Centrifuge and try the solubility of the precipitate in dilute HCl or dilute HNO_3 (?).

(*b*) *Silicon Tetrafluoride.*—Thoroughly mix a pinch of powdered CaF_2 with a like amount of powdered SiO_2. Introduce the mixture into a dry test tube and add 1 drop of concentrated H_2SO_4. In the mouth of the test tube, place a cork that has been slotted (so that it will not be airtight) and fitted with a short length of glass tubing (Fig. 15). Dip the tubing in water, so that it will carry a drop of water on its lower end. Warm the reaction mixture, if needed, and note the reaction in the drop of water. Complete the following equations: $CaF_2 + H_2SO_4 \rightarrow ? + ?$; $HF + SiO_2 \rightarrow ? + ?$; and $SiF_4 + H_2O \rightarrow H_2SiF_6 + Si(OH)_4$.

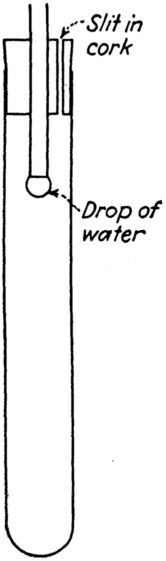

FIG. 15.—Apparatus for the drop-of-water test.

(114) Fluosilicate, SiF_6^{--}. (*a*) *Barium Fluosilicate.*—Dilute 1 drop of fluosilicic acid, H_2SiF_6, and add 1 drop of $Ba(NO_3)_2$ solution (?, E).

(*b*) *Potassium Fluosilicate.*—Dilute 1 drop of H_2SiF_6 and add 1 drop of KCl solution (?, E).

Note.—K_2SiF_6 is slightly soluble in water. The precipitation can be made quantitative by adding an equal volume of alcohol to the mixture.

(*c*) *Decomposition of Fluosilicic Acid.*—Place 1 drop of H_2SiF_6 in a crucible and add 1 drop of concentrated H_2SO_4. Hold a stirring rod that has just been dipped in water in the fumes (?). (*Caution:* Do not inhale.) The turbidity is caused by $Si(OH)_4$. Complete and balance: $H_2SiF_6 \rightarrow ? + ?$; $SiF_4 + HOH \rightarrow Si(OH)_4 + ?$

Dilute 1 drop of H_2SiF_6 and add several drops of NH_4OH (excess) (?). The precipitate is $Si(OH)_4$. Complete and balance: $H_2SiF_6 + NH_4OH \rightarrow Si(OH)_4 + ? + ?$

(115) Sulfate, SO_4^{--}. (*a*) *Barium Sulfate.*—Dilute 1 drop of dilute H_2SO_4 and add 1 drop of $Ba(NO_3)_2$ or $BaCl_2$ solution (?, E). Centrifuge and try the solubility of the precipitate in HNO_3 or HCl (?).

Note.—$BaCl_2$ solution is commonly used as a reagent for SO_4^{--}, but in general unknowns $Ba(NO_3)_2$ seems preferable for the following reason:

With Ag^+, Hg_2^{++}, and Pb^{++}, $BaCl_2$ precipitates insoluble chlorides which might be mistaken for $BaSO_4$. $Ba(NO_3)_2$, on the other hand, may be used in all cases, since all nitrates are soluble.

(*b*) *Calcium Sulfate.*—Dilute 1 drop of H_2SO_4 and add $CaCl_2$ dropwise in slight excess. Centrifuge and reject the precipitate. To the solution add 1 drop of $Ba(NO_3)_2$ or $BaCl_2$ solution (?, E). (DIFFERENCE BETWEEN SO_4^{--} AND F^-.)

Note.—The separation of F^- from SO_4^{--} by means of Ca^{++} is not quantitative, for much of the SO_4^{--} is carried down by the CaF_2 as $CaSO_4$. However, enough SO_4^{--} remains in solution to be easily detected by Ba^{++}.

(*c*) *Reduction of Sulfate by Charcoal.*—Mix a pinch of an insoluble sulfate (*e.g.*, $CaSO_4$ or $BaSO_4$) with an excess of powdered charcoal and add a little solid Na_2CO_3. Heat the mixture to low redness in a crucible for several minutes. Let the crucible cool, acidify the residue with a few drops of dilute HCl, and promptly cover the crucible with a filter paper moistened with 1 drop of $Pb(C_2H_3O_2)_2$ solution. Balance the equations: $CaSO_4 + C\ (+\ \text{heat}) \rightarrow ? + ?$; $CaS + H^+ \rightarrow ? + ?$.

Exercises

1. Is a precipitate with $BaCl_2$ solution, insoluble in water and HNO_3, a test for SO_4^{--}? Recall the reaction between $BaCl_2$ and $AgNO_3$ solutions. Cite two other similar cases.
2. A neutral solution gives no precipitate with $AgNO_3$ solution but with $Ba(NO_3)_2$ solution gives a white precipitate, insoluble in dilute HNO_3 and soluble in excess of concentrated HNO_3. What anion is suggested?
3. Write equation for the hydrolysis of SiF_4.
4. Explain the precipitation of $Ba(NO_3)_2$ from $Ba(NO_3)_2$ solution by adding concentrated HNO_3.
5. Can F^- be separated from SO_4^{--} by Ca^{++}? by Ba^{++}?
6. State just how the presence of water interferes with the formation of SiF_4 when a mixture of SiO_2, CaF_2, and dilute H_2SO_4 is warmed.

GROUP VI

This group contains the various silicates, which give, upon acidification, precipitates of silicic acid. The formula for silicic acid is written in several ways, *viz.*, H_2SiO_3, H_4SiO_4 or $Si(OH)_4$, $SiO_2.2H_2O$, etc.

Silicate anions give precipitates with Ag^+ and Ba^{++}, but these reactions are not specific. All the silicates are insoluble except the alkaline silicates, Na_2SiO_3 and K_2SiO_3.

PRELIMINARY EXPERIMENTS

(116) Silicate, SiO_3^{--}, SiO_4^{----}, Etc. (*a*) *Precipitation of Silicic Acid.*—Put 1 drop of Na_2SiO_3 solution ("water glass") in a test tube, and dilute it to 1 ml. and shake well. Add 1 drop of dilute HCl (?, E). Try the solubility of the precipitate in HCl or HNO_3 (?). Evaporate the mixture to dryness on a watch glass over a beaker of boiling water, and reserve the residue for the next experiment.

(*b*) *Solubility of Silica in Fused Sodium Carbonate.*—(Instructions.) Make a loop in a clean platinum wire, heat it to redness, and bring the hot wire into contact with some anhydrous Na_2CO_3 on a watch glass. Heat the wire again and add more Na_2CO_3. Continue the operation until a bead about the size of a small grain of rice is built up. Moisten the bead with a drop of water and bring it into contact with a minute amount of the residue reserved from the preceding experiment. Reheat until the bead is perfectly transparent. Explain the effervescence by completing the equation: $Na_2CO_3 + SiO_2 \rightarrow ? + ?$.

Note.—The platinum wire may be easily cleaned by heating the bead to redness and dipping the bead into cold water. The bead is shattered, and the fragments may be easily separated from the wire without injuring it.

(*c*) *The "Silica Skeleton."*—Prepare a bead as in the preceding experiment, using $NaNH_4HPO_4$ (microcosmic salt) instead of Na_2CO_3. Upon heating, the material loses NH_3 and H_2O (E), leaving a glassy bead of sodium metaphosphate, $NaPO_3$. Add a little SiO_2 as in (*b*) and reheat. Does the SiO_2 dissolve? The opaque mass is known as a "silica skeleton."

Exercises

1. An alkaline solution gives, upon acidification with HCl, a white gelatinous precipitate, insoluble in NaOH solution after evaporation. Identify the anion.
2. What difference in property of the acid anhydrides accounts for the fact that SiO_2 will dissolve in the Na_2CO_3 bead but not in the $NaPO_3$ bead?

Systematic Analysis of Anions

In cation analysis, the separation of an ion must precede its detection. In anion analysis, on the other hand, ions are detected, as far as possible, without separating them from other anions. There are certain tests, however, in which interferences occur, and in these cases the interfering ions must be removed before the test can be applied. To illustrate: The precipitation-of-AgCl test for Cl^- cannot be used in the presence of Br^-; nor the brown-ring test for NO_3^- in the presence of I^-.

The procedures used in this manual consist of two general steps: (1) The elimination of ions that could not exist in the substance under examination. For example, I^- could not exist in an oxidizing medium, nor CO_3^{--} in an acid medium. (2) The anions are divided into groups by means of group reagents, and no tests are made for an anion when its group is definitely indicated to be absent. For example, S^{--} ions could not be present in a solution that does not form a precipitate with $AgNO_3$ solution.

As seen below, there are other ways of reducing possibilities in an anion analysis.

GENERAL PROCEDURES

Owing to numerous interferences and in order to take advantage of short cuts, anion analysis cannot be reduced to routine methods similar to those used in cation analysis. A more flexible procedure is followed, calling upon the student to use his discretion at many points.

Two general procedures may be outlined, depending on whether the unknown material is a solution (Case I) or a solid (Case II).

Case I.—The Unknown Is a Solution.

Use 1- or 2-drop portions for the following tests:

(117) The Presence of Free Acids.—To 1 ml. of water add 1 drop of methyl orange solution and 1 drop of the unknown solution. A change in color from yellow to red indicates the presence of *free acids*. The following anions may be assumed to be absent from solutions that are definitely acid: CN^-, S^{--}, NO_2^-, CO_3^{--}, SO_3^{--}, $S_2O_3^{--}$, ClO_3^-, SiO_3^{--}.

In case of colored solutions, litmus paper may be used instead of methyl orange solution. A red color indicates free acids.

Notes.—1. The approximate nature of this evidence must be emphasized. Several of the above anions form acids that are fairly stable in dilute solution, *e.g.*, H_2CO_3, H_2SO_3, HNO_2, etc.

2. Certain normal salts, sometimes called "neutral salts," form solutions that are definitely acidic or basic, owing to hydrolysis; *e.g.*, $CuSO_4$ solution is slightly acidic, and Na_3PO_4 solution is decidedly basic.

(118) Oxidizing Agents.—To a few drops of a solution of $MnCl_2$ in concentrated HCl add 1 drop of the unknown solution. A brown-to-black color indicates the presence of *oxidizing agents.* The following anions of reducing acids are probably absent: I^-, $Fe(CN)_6^{----}$, S^{--}, SO_3^{--}, $S_2O_3^{--}$.

(119) Reducing Agents.—Mix 1 drop of $FeCl_3$ and 1 drop of $K_3Fe(CN)_6$ solution and dilute slightly. The $K_3Fe(CN)_6$ solution should be freshly prepared, so as to avoid the presence of $Fe(CN)_6^{----}$ ions. To the brown mixture add a drop of the unknown solution. A blue color indicates the presence of *reducing agents.* The following ions are therefore probably absent: $Fe(CN)_6^{---}$, CrO_4^{--}, $Cr_2O_7^{--}$, NO_3^-, ClO_3^-, and MnO_4^-.

Notes.—1. Certain weak reducing agents may coexist in the same solution with weak oxidizing agents, *e.g.*, $C_2O_4^{--}$ and NO_3^-, or SCN^- and Fe^{+++}.

2. Salts of certain oxidizing acids and reducing acids may be mixed without reaction. For example, a mixture of KNO_3 and KI is stable in a neutral or alkaline solution. Upon acidification, however, reaction takes place. An easy explanation of this case is that the HNO_3 molecule is an oxidizing agent, while the NO_3^- ion is not.

3. The NO_2^- ion functions as a reducing agent toward strong oxidizing agents (*e.g.*, $HMnO_4$), and as an oxidizing agent toward strong reducing agents (*e.g.*, HI). Its activity in these dual roles is not sufficient for it to give definite or decisive reactions with either of the above reagents for oxidizing and reducing constituents.

(120) Acidification with Dilute Acids.—Place 1 or 2 drops of the unknown solution in a test tube and add 1 drop of dilute HNO_3. Effervescence indicates the presence of anions of *volatile* or *unstable acids*, such as S^{--}, NO_2^-, CO_3^{--}, and $S_2O_3^{--}$. The failure to effervesce does not positively exclude the presence of small amounts of these anions, for the corresponding acids are slightly soluble in water.

The formation of a precipitate indicates the presence of anions of unstable acids; *e.g.*, $S_2O_3^{--}$ gives S, or SiO_3^{--} gives $Si(OH)_4$.

(121) Reaction with Concentrated Sulfuric Acid.—Place 1 or 2 drops of the solution in a small casserole and evaporate to bare dryness over a small flame. After cooling, add 1 drop of concentrated H_2SO_4 and heat, if necessary, to start the reaction. The reactions are summarized in the following table:

Colorless gas	Colored gas		No reaction
	Color	Anions indicated	
Cl^-	Yellow	ClO_3^-	BO_3^{---}
CN^-			PO_4^{---}
SCN^-		Br^-	AsO_3^{---}
$Fe(CN)_6^{----}$	Red brown	NO_2^-	AsO_4^{---}
$Fe(CN)_6^{---}$		NO_3^-	CrO_4^{--}
S^{--}	Purple	I^-	$Cr_2O_7^{--}$
$C_2H_3O_2^-$			SO_4^{--}
CO_3^{--}			SiO_3^{--}
$C_2O_4^{--}$			
SO_3^{--}			
$S_2O_3^{--}$			
NO_3^-			
F^-			

(122) Determination of Anion Groups.—Dilute 2 drops of the unknown solution to 1 ml. and add $AgNO_3$ solution in slight excess. If a precipitate forms, add a few drops of dilute HNO_3. Note carefully whether any precipitate dissolves. A precipitate insoluble in dilute HNO_3 indicates the presence of *Group I*. A precipitate soluble in dilute HNO_3 indicates the presence of *Group III* or possibly *Group II*.

Note.—If the acid filtrate from the Group I precipitation is carefully neutralized by the dropwise addition of NH_4OH, the presence of Group III is frequently shown by the appearance of a precipitate. This precipitate dissolves promptly in the excess NH_4OH, and its presence must be caught at just the right moment. Another recourse is to evaporate the excess NH_4OH on a water bath and thereby regain the elusive precipitate. This method for detecting Group III is not generally recommended, not only because of the difficulty in obtaining the precipitate but more particularly because certain anions of the group were destroyed upon acidification. NaOH cannot be used instead of NH_4OH, since excess NaOH precipitates AgOH or Ag_2O.

Dilute 2 drops of the unknown solution to 1 ml. and add $Ba(NO_3)_2$-$Ca(NO_3)_2$ mixture in slight excess. If a precipitate forms, add a few drops of dilute HNO_3 and note whether any of the precipitate dissolves. A precipitate insoluble in dilute HNO_3 indicates the presence of *Group V.* A precipitate soluble in HNO_3 indicates the presence of *Group III.*

If Group V is present, centrifuge the acidified solution, decant, and carefully neutralize the decantate with NH_4OH. The formation of a precipitate indicates *Group III.* This test is not always so sensitive as desired.

Note.—A combination of Ba^{++} and Ca^{++} ions is used in the detection of Groups V and III, because Ba^{++} is the more sensitive reagent for certain anions, and Ca^{++} the more sensitive reagent for other anions.

It will be noted that there are positive tests for the presence of Groups I and V in all cases and for Group III in some cases, but none for Groups II and IV in any case. Therefore special tests should be made for all members of Groups II and IV in all unknowns except where their presence is definitely excluded by other evidence. Group VI gives no definite reaction with Ag^+ or Ba^{++}-Ca^{++}, and the presence of this group (silicates) must be determined by special tests.

(123) Significance of the Cations Present in the Solution.—Refer to the Table of Solubilities (pages 148–151), and list the anions that could be present in a substance of the solubility found above and containing the cations found in cation analysis.

To illustrate, if Ag^+ has been found to be present in a neutral solution, the only anion possibilities are NO_3^-, ClO_3^-, MnO_4^-, SO_4^{--}, F^-, and small amounts of $C_2H_3O_2^-$ and NO_2^-. A definitely acid solution may contain, in addition to the anions forming water-soluble salts, also anions forming acid-soluble salts. For example, if Ag^+ is present, an acidic solution may contain, in addition to the above, $C_2O_4^{--}$, BO_3^{---}, PO_4^{---}, AsO_4^{---}, AsO_3^{---}, and $Cr_2O_7^{--}$.

Note.—An important exception to this principle is to be noted in cases where cations and anions form soluble compounds of low ionization. For example, a Pb^{++} solution may contain SO_4^{--} if $C_2H_3O_2^-$ is also present; or a Mg^{++} solution may contain CO_3^{--} if NH_4^+ is also present.

(124) Removal of Interfering Cations.—There are certain cases where cations interfere with anion tests. Examples are: If a solution contains Ag^+, a precipitate of AgCl will be obtained when $BaCl_2$ is added, thereby giving a false test for SO_4^{--} Trivalent cations tend to precipitate $C_2H_3O_2^-$ ions as basic acetates in neutral and alkaline solutions, resulting in a loss of this anion. Colored cations in general interfere with color tests. Ba^{++}, Sr^{++}, Ca^{++}, and Pb^{++} interfere with the brown-ring test for NO_3^- by forming precipitates of insoluble sulfates, which in some way hinder the formation of brown $FeSO_4.NO$.

Therefore, before starting the analysis for anions, the identity of the cations present in the substance must be known. In other words, a cation analysis must precede an anion analysis. In general, the members of Cation Groups I, II, III, and IV are apt to cause trouble, and it is desirable that they should be removed, leaving in solution the alkali cations only. This removal of cations is usually carried out by precipitation with Na_2CO_3 as follows:

Place about 2 ml. of the solution in a small beaker and add 1 ml. of concentrated Na_2CO_3 solution. Mix well and transfer the mixture to a test tube and heat in a water bath for about 1 min. Centrifuge and wash the precipitate with a little water. The combined centrifugate (called the *prepared solution*) retains the anions of the unknown, while the residue contains the cations of Groups I to IV in the form of carbonates, hydroxides, etc. Reserve this solution for use in special tests, as called for.

This prepared solution is not suitable for use in all anion tests. The violent effervescence which occurs upon acidification interferes seriously with the tests for anions of volatile and unstable acids. It is better to test for such anions on portions of the original unknown.

Note.—The Na_2CO_3 reagent frequently furnished for this procedure is Solvay soda and contains small amounts of Cl^- ions. For this reason, the Na_2CO_3 should always be tested for Cl^- by $AgNO_3 + HNO_3$, and allowance made for this impurity.

An alternate procedure is to keep in mind the cations present and either remove them by appropriate methods as necessary or choose anion tests that are not subject to interference.

Case II.—The Unknown Is a Solid.

If the substance is a metal or alloy, proceed to (**163**); if it is not a metal or alloy, grind it finely in a mortar and use small portions for the following tests as directed:

(**125**) **Solubility.** (*a*) *In Water.*—Place a pinch of the solid in a test tube, add 1 ml. of water, and warm in a water bath. If there is no apparent effect, proceed to (*b*). If partial solubility is indicated, wash the residue with more water and add the washings to the main solution. Treat this solution by Case I, page 103, and reserve the residue for (*b*).

(*b*) *In Acids.*—To the material insoluble in water, add 1 ml. of dilute HNO_3 and heat in the water bath. A yellow gummy residue, tending to float in the hot acid solution, sometimes separates. Filter and test the precipitate for free sulfur by (**135,** *C*). A separation of sulfur indicates the presence of sulfide or thiosulfate. A white, amorphous precipitate may be stannic oxide, $SnO_2.xH_2O$, or silicic acid, $SiO_2.xH_2O$. This precipitate should be separated and tested for Sn by (**42**) and SiO_2 by (**160,** *B*).

If the solvent action of HNO_3 is not satisfactory, HCl or aqua regia should be tried.

Recall that certain anions are destroyed upon acidification, and that tests for them must be made on the original substance.

Notes.—1. The method of selective solution (*i.e.*, successive extraction by water, acids, and other solvents) is an excellent procedure for the analysis of mixtures containing both soluble and insoluble constituents. The constituents soluble in each solvent are completely extracted, giving two or more simple unknowns in the place of one complex one. In addition, this method gives information about the actual ingredients used in making up the mixture.

2. The residue insoluble in acids consists of such materials as AgCl, $BaSO_4$, $PbSO_4$, complex cyanides (*e.g.*, Prussian blue, Turnbull's blue), insoluble silicates, etc.

3. There are a few substances for which HCl or aqua regia are better solvents than HNO_3, *e.g.*, SnS_2.

(**126**) **Tests on the Original Solid.**—Use very small portions of the pulverized solid for the following tests:

(*a*) *Anions of Volatile or Unstable Acids.*—Place a pinch of the substance in a test tube and add 1 drop of concentrated H_2SO_4. [See (**121**) for interpretation.]

(*b*) *Sulfite and Thiosulfate.*—Test a small portion for SO_3^{--} and $S_2O_3^{--}$ by the evolution-of-SO_2 test (**144**).

(*c*) *Carbonate.*—Test a third portion for CO_3^{--} by the evolution-of-CO_2 test, preferably using the absorption trap (**145**).

(*d*) *Sulfide.*—Test a fourth portion for S^{--} by the evolution-of-H_2S test, using $Zn + H_2SO_4$ as the reagent (**135**).

(*e*) *Sulfate.*—In the absence of SCN^-, S^{--}, SO_3^{--}, and $S_2O_3^{--}$, a fifth portion may be tested for SO_4^{--} by the reduction-to-sulfide reaction. [See (**159,** *B*).]

(*f*) *Fluoride.*—Use a sixth portion to test for F^- by the hydrolysis-of-SiF_4 test. [See (**158,** *B*).]

(127) Tests of the H_2SO_4 Solution.—Dilute H_2SO_4 is a favorable medium for several tests. Shake about 0.02 gram of the powdered substance with 1 ml. of cold dilute H_2SO_4 and add about 4 ml. of water. Decant from any residue and divide into small portions for the following tests:

(*a*) *Acetate.*—Test one portion for $C_2H_3O_2^-$ by the ethyl acetate test (**141**), or, in the presence of interferences, by the $La(NO_3)_3$ test.

(*b*) *Nitrite and Nitrate.*—To a second portion add a drop of $FeSO_4$ solution. [See (**140**).] If the test is negative, introduce concentrated H_2SO_4 below the solution. A brown ring indicates NO_3^- (**152,** *b*).

(*c*) *Iodide.*—Test a third portion for I^- by adding Cl_2 and CCl_4 and shaking. [See (**137**).]

(*d*) *Bromide.*—From a fourth portion remove I^- (if present) by means of $NaNO_2$ and test for Br^- by $Cl_2 + CCl_4$ by (**137**).

(*e*) *Chloride.*—If SCN^- is present, remove it by ignition with MnO_2 (**138,** *A*); if I^- is present, remove it by (**137**). Then test for Cl^- in the presence of Br^- by means of the $AgNO_3$-NaOH procedure (**138,** *B*).

(*f*) *Chlorate and Perchlorate.*—If any ions of Anion Group I are present, remove them by $AgNO_3$. Test the filtrate for ClO_3^- by warming with Zn and adding $AgNO_3$ (**153**). Then convert any ClO_4^- to Cl^- by ignition with MnO_2 (**154**). The presence of Cl^- in the residue indicates ClO_4^-.

(128) Tests on the HNO_3 Solution.—Warm about 0.05 gram of the powdered solid with 1 ml. of dilute HNO_3 and dilute the mixture to about 3 ml. Reserve any residue for (**164**). Divide the solution and test portions of it as follows:

(*a*) *Phosphate.*—Use one portion for the $(NH_4)_2MoO_4$ test for PO_4^{---}. [See (**149**).]

(*b*) *Fluosilicate.*—Test a second portion for SiF_6^{--} by KCl + alcohol (**157**) and confirm any precipitate by the decomposition-of-H_2SiF_6 test.

(*c*) *Fluoride.*—Test a third portion for F^- by adding $Ca(NO_3)_2$ and confirming any precipitate by (**158**).

(*d*) *Sulfate.*—Test the filtrate from any CaF_2 precipitate in (*c*) above for SO_4^{--} by (**159**).

(**129**) **Tests on the HCl Solution.**—Warm about 0.05 gram of the powdered substance with 1 ml. of dilute HCl and add 2 ml. of water. Centrifuge and reserve any residue for (**164**). Divide the solution into four portions and test them as follows:

(*a*) *Thiocyanate.*—Test one portion for SCN^- by the $FeCl_3$ reaction (**133**).

(*b*) *Ferrocyanide.*—Test a second portion for $Fe(CN)_6^{----}$ by the Prussian blue reaction with $FeCl_3$ (**133**).

(*c*) *Ferricyanide.*—Test a third portion for $Fe(CN)_6^{---}$ by the Turnbull's blue reaction with $FeSO_4$ (**134**).

(*d*) *Borate.*—In the presence of Cu^{++} and Ba^{++}, use the remainder for a turmeric paper test for BO_3^{---} (**147**).

(**130**) **Tests in Cation Analysis.**—The detection of the following anions is based on reactions met during the analysis for cations.

(*a*) *Arsenite and Arsenate.*—AsO_3^{---} and AsO_4^{---} are indicated by the detection of As in neutral or alkaline solutions.

(*b*) *Chromate and Dichromate.*—CrO_4^{--} and $Cr_2O_7^{--}$ are indicated by the reduction of $Cr_2O_7^{--}$ by H_2S in Group II, and the detection of Cr in Group III.

(*c*) *Permanganate.*—MnO_4^- is indicated by the bleaching of a purple color by H_2S in Group II and by the detection of Mn in Group III.

(**131**) **Decomposition by Sodium Carbonate.**—Another method for effecting the solution of the anions in water-insoluble unknowns is as follows:

Place about 0.5 gram of the finely divided solid in a test tube and add about 5 ml. of concentrated Na_2CO_3 solution. Heat in a water bath for 5 min., stirring the mixture frequently. Centrifuge and wash the residue. The filtrate (called the

Table XII.—Elimination of Anions by Means of Their Reactions with Various Reagents

Anions	The original is an acid solution	The unknown does not effervesce with dilute HNO_3	The solution from the preceding column gives no reaction with $AgNO_3$	An HNO_3 solution of the unknown gives no reaction with $Ba(NO_3)_2$	The solution from the preceding column gives no reaction with NaOH	An HCl solution of the unknown gives no darkening with $MnCl_2$ + HCl	An HCl solution of the unknown gives no blue color with $FeCl_3$ + $K_3Fe(CN)_6$	The original evolves no gas with concentrated H_2SO_4 + heat	Summary
Cl^-	....	....	Absent	....	....	....	....	Absent ✓	
Br^-	....	....	Absent	....	....	....	....	Absent ✓	
I^-	....	....	Absent	....	....	....	Absent	Absent ✓	
CN^-	Absent	....	Absent	....	....	....	....	Absent	
$Fe(CN)_6^{----}$	....	....	Absent	....	....	....	Absent	Absent	
$Fe(CN)_6^{---}$	....	....	Absent	....	....	Absent	....	Absent	
SCN^-	....	....	Absent	....	....	....	....	Absent	
S^{--}	Absent	Probably absent	Probably absent	....	....	....	Absent	Absent ✓	
NO_2^-	Absent	Absent	....	....	....	Probably absent	Absent	Absent	
$C_2H_3O_2^-$	....	....	....	....	....	....	....	Absent ✓	
CO_3^{--}	Absent	Absent	....	....	....	....	....	Absent ✓	
$C_2O_4^{--}$	....	....	....	....	Absent	....	....	Absent	
SO_3^{--}	Absent	Absent	....	....	....	....	Absent	Absent	
$S_2O_3^{--}$	Absent	Absent	....	....	....	....	Absent	Absent	
BO_3^{---}	....	....	....	....	Probably absent				
$C_4H_4O_6^{--}$	....	....	....	....	Absent	....	....	Absent	
PO_4^{---}	....	....	....	....	Absent				
AsO_4^{---}	....	....	....	....	Absent				
AsO_3^{---}	....	....	....	....	Absent				
CrO_4^{--}	....	....	....	....	Absent	Absent			
NO_3^-	....	....	....	....	....	Absent	....	Absent	
ClO_3^-	Absent	....	....	....	....	Absent	....	Absent	
ClO_4^-									
MnO_4^-	....	....	....	....	....	Absent			
SO_4^{--}	....	....	....	Absent					
F^-	....	....	....	Absent	....	....	....	Absent	
SiO_3^{--}	Absent								

"*prepared solution*") retains the anions of the unknown, while the residue contains the cations of Groups I to IV in the form of carbonates, hydroxides, etc. Analyze the Na_2CO_3 solution by (**118**), (**119**), (**122**), and (**132**) to (**159**). Remember that the presence of Na_2CO_3 interferes with certain of these tests. [See (**124**), page 107.] Analyze the residue for cations by (**19**) to (**85**).

Notes.—1. The action of Na_2CO_3 in decomposing insoluble materials is a mass effect. Illustrating by $CaSO_4 + CO_3^{--} \rightleftarrows CaCO_3 + SO_4^{--}$, an excess of Na_2CO_3 favors the forward reaction, converting $CaSO_4$ into $CaCO_3$ with practical completeness. The net result is the displacement of the acid radical by CO_3^{--}, bringing the former into solution as an Na^+ salt.

2. There are some salts of high insolubility that are only slightly decomposed by digestion with Na_2CO_3 solution, *e.g.*, the sulfides of Groups I and II, the halides of Ag^+ and Hg_2^{++}, certain phosphates of Groups III and IV, $BaSO_4$, etc. This limitation must be kept in mind, and tests for these anions made on the original.

GROUP I

(**132**) **Test for the Group.**—Dilute 1 drop of the original solution to 1 ml. and add 1 drop of dilute HNO_3 and 1 drop of $AgNO_3$ solution. A precipitate indicates the presence of Anion Group I. Note the color of the precipitate and try to interpret it. Centrifuge or filter, wash the precipitate, and try its solubility in NH_4OH. A white precipitate, soluble in NH_4OH, indicates Cl^-, CN^-, SCN^-, or $Fe(CN)_6^{---}$; a black precipitate indicates S^{--}. Test samples of the solutions by procedures (**133**) to (**138**). If there is no precipitate, proceed to Group II.

(**133**) **Thiocyanate and Ferrocyanide.**—Dilute 1 drop of the solution to about 1 ml., acidify the mixture with 1 drop of dilute HCl, and add 1 drop of $FeCl_3$ solution. A blue precipitate of Prussian blue indicates *ferrocyanide;* a reddish color, SCN^- or I^-. To the red solution, add about 0.5 ml. of CCl_4 and shake well. If the layers do not separate, centrifuge. A violet color in the CCl_4 layer indicates iodide; a blood-red color in the water layer indicates *thiocyanate.*

(**134**) **Ferricyanide.**—Dilute a drop of the solution to 1 ml., acidify with a drop of dilute HCl, and add 1 drop of freshly prepared $FeSO_4$ solution. A blue precipitate of Turnbull's blue indicates *ferricyanide.*

Note.—Upon standing, $FeSO_4$ solution is oxidized by the air to $Fe_2(SO_4)_3$ which, in the presence of $Fe(CN)_6^{----}$, interferes with the test for $Fe(CN)_6^{---}$.

(135) **Sulfide.**—Two cases are to be considered.

A. The Unknown Is a Solution, or a Solid Soluble in Water.—S^{--} ions may be assumed to be absent from soluble unknowns unless the solution is alkaline. This follows from the volatility of H_2S from acid solutions.

Place a drop of the solution in a crucible, acidify with 1 or 2 drops of dilute HCl, and cover the crucible with a filter paper to which has been added 1 drop of $Pb(C_2H_3O_2)_2$ solution. A brown-to-black stain of PbS indicates the presence of sulfide.

B. The Unknown Is a Solid Insoluble in Water.—Be sure that the material contains no constituent soluble in water, since certain ions (*e.g.*, SCN^- and $S_2O_3^{--}$) evolve H_2S when treated with HCl + Zn.

Place a small portion of the powdered unknown in a crucible, add a few drops of dilute HCl, and test for H_2S with $Pb(C_2H_3O_2)_2$ as in *A*. If the solid is insoluble in dilute HCl, add a pinch of zinc dust. Sulfides insoluble in HCl dissolve in HCl + Zn with the liberation of H_2S. A brown-to-black stain on the $Pb(C_2H_3O_2)_2$ paper indicates the presence of *sulfide.*

C. Test for Free Sulfur.—Place a little of the substance in contact with a bright silver coin in a small casserole and warm with dilute NaOH solution. The formation of a black stain on the coin indicates *free sulfur.*

(136) **Separation of the Halide Ions.**—Certain ions of this group—particularly S^{--}, $Fe(CN)_6^{----}$, and $Fe(CN)_6^{---}$—interfere with the tests for Cl^-, Br^-, and I^-. They are therefore removed by precipitation with Co^{++} solution.

In a large test tube, place 0.5 ml. of the unknown solution and 0.5 ml. of concentrated $Co(NO_3)_2$ solution. Now add dropwise dilute Na_2CO_3 solution (free from NaCl) until the solution is slightly alkaline (litmus test). Centrifuge or filter, and wash the residue twice with 1-ml. portions of water. Reject the precipitate and use the solution for the following tests.

Notes.—1. Cd^{++} might also be used to remove S^{--}, $Fe(CN)_6^{----}$ and $Fe(CN)_6^{---}$.

2. An excess of $Co(NO_3)_2$ solution must be used. Upon neutralizing the solution, the anions are precipitated in the order of their insolubility, *viz.*, first, the complex cyanides; next, CoS; and last, $CoCO_3$.

(137) Iodide and Bromide.—Acidify one-third of the solution from **(124)** with H_2SO_4 and add 1 ml. of CCl_4 and 2 or 3 drops of Cl_2 solution. Shake well. A violet color in the CCl_4 layer indicates the presence of *iodide*. A yellow-brown color indicates that iodide is absent and that *bromide* is present. A colorless layer indicates that both iodide and bromide are absent.

If I^- is found, place a second third of the solution in a large test tube and add 2 drops of $NaNO_2$ solution. Acidify the solution with dilute H_2SO_4 and boil until the solution is just colorless. This will expel free I_2 and also any colored decomposition products of HNO_2. Add another drop of $NaNO_2$ to test for the completeness of the reaction. To the I^--free solution add about 0.5 ml. of CCl_4, and then Cl_2 dropwise. Shake well. A yellow-brown color in the CCl_4 layer indicates the presence of *bromine*.

(138) Chloride.—Test the remaining third of the solution reserved from **(136)** for Cl^- as follows:

A. Removal of Thiocyanate.—If SCN^- was found to be absent in **(133)**, proceed directly to *B*. If SCN^- is present, transfer to a casserole and add 2 or 3 drops of $Mn(NO_3)_2$ and enough Na_2CO_3 to make the mixture alkaline. Evaporate to dryness and carefully ignite until the whole mass is black. Allow to cool and add 2 or 3 ml. of water. Warm and filter. Proceed to *B*.

B. Removal of Bromide and Iodide.—To the solution from above, add $AgNO_3$ in slight excess. Centrifuge and wash the precipitate. Warm the precipitate with 2 or 3 ml. of 0.1 per cent NaOH for several minutes in a water bath, with frequent shaking, so as to break down lumps in the precipitate. Decant or filter, acidify the decantate with HNO_3, and add 1 or 2 drops of $AgNO_3$. A white turbidity of AgCl indicates the presence of *chloride*.

(139) Thiosulfate.—Strictly speaking, $S_2O_3^{--}$ is a member of Anion Group III, for both $Ag_2S_2O_3$ and BaS_2O_3 are insoluble in water but soluble in dilute HNO_3. However, $Ag_2S_2O_3$ tends to decompose into Ag_2S, insoluble in dilute HNO_3, so that Group I appears to be indicated.

See **(144)** for directions for testing for $S_2O_3^{--}$

TABLE XIII.—ANALYSIS OF ANION GROUP I

(**132**) To a portion of the original solution, add HNO_3 and $AgNO_3$. Precipitate: Group I. Centrifuge or filter. Try the solubility of the precipitate in NH_4OH. Residue indicates the presence of I^-, $Fe(CN)_6^{---}$, or S^{--}.

(**133**) Acidify a portion of the original solution with HCl and add $FeCl_3$. Blue precipitate of $Fe_4(Fe(CN)_6)_3$ indicates $Fe(CN)_6^{----}$; red solution, SCN^- or I^-. Extract red solution with CCl_4. Violet color in CCl_4 layer indicates I^-; blood-red color in the water layer indicates SCN^-.

(**134**) Acidify a portion of the original with HCl and freshly prepared $FeSO_4$ solution. Blue color of $Fe_3(Fe(CN)_6)_2$ indicates $Fe(CN)_6^{---}$.

(**135**) Test original with litmus paper. If alkaline, acidify a portion in a crucible with HCl and cover with $Pb(C_2H_3O_2)_2$ paper. Brown-black stain indicates S^{--}. If original is a solid, insoluble in water, place small portion in a crucible, add HCl, and cover with $Pb(C_2H_3O_2)_2$ paper. Brown stain indicates S^{--}. If there is no reaction, add Zn dust. Brown-black stain indicates insoluble sulfide.

(**136**) If S^{--}, $Fe(CN)_6^{----}$, or $Fe(CN)_6^{---}$ is present, add $Co(NO_3)_2$ and Na_2CO_3. Wash and reject precipitate. Divide filtrate into three portions.

(**137**) Acidify the first portion with H_2SO_4 and add Cl_2, CCl_4. A purple CCl_4 layer indicates I^-, a yellow-brown layer indicates Br^-, and a colorless layer indicates absence of I^- and Br^-. If I^- is found, remove it from the second portion by boiling with $NaNO_2 + H_2SO_4$. Add Cl_2 and CCl_4 and centrifuge. A yellow color in the CCl_4 layer indicates Br^-.

(**138**) *A*. If SCN^- is present, remove it from the remaining portion by evaporating and igniting the residue with $Mn(NO_3)_2 + Na_2CO_3$. Extract residue with warm water, and proceed to *B*.

B. To solution free from SCN^-, add $AgNO_3$. Centrifuge, wash precipitate, and centrifuge with warm 0.1 per cent NaOH. Acidify decantate with HNO_3 and add $AgNO_3$. White precipitate of AgCl indicates Cl^-.

GROUP II

Owing to the appreciable solubility of $AgC_2H_3O_2$ and $AgNO_2$ in water, the group reagents may fail to indicate the presence of the group. It is well, for this reason, to treat this group as a division of Group IV, and to make tests for its members on all unknowns, except those that are completely insoluble in warm water.

(140) Nitrite.—Test the original solution for the presence of free acids, using methyl orange as the reagent. NO_2^- ions may be assumed to be absent from unknowns that are definitely acid.

Dilute 1 or 2 drops of the original solution and add 1 drop of $FeSO_4$ solution acidified with H_2SO_4. A brown color indicates the presence of *nitrite.* This color is visible in the presence of most colored ions, such as CrO_4^{--}, Fe^{+++}, etc.

Notes.—1. Carbonates, sulfites, etc., which effervesce upon acidification, interfere with this test. These ions should be removed by precipitating with $BaCl_2$ or $Ba(NO_3)_2$ and making the test on the decantate or filtrate.

2. Iodides interfere by reacting, upon acidification, with the anions of oxidizing acids, forming free iodine. If present, I^- ions should therefore be removed by $AgNO_3$ or Ag_2SO_4 before trying this test.

Acidify a small amount of the unknown in a small beaker with dilute H_2SO_4 and warm gently. Cover with a watch glass carrying on its lower side a piece of starch-iodide paper. A blue color indicates nitrite (in the absence of ClO_3^-, peroxides, etc.).

Note.—Nitrites, upon acidification, give off $NO_2 + NO$, and the former oxidizes I^- to I_2, which turns starch blue. This test is not specific, since all volatile oxidizing agents behave similarly.

(141) Acetate.—Treat a small amount of the unknown (solution or powder) in a beaker with a few drops of concentrated H_2SO_4, and cautiously smell the fumes evolved. *Be sure that cyanides are absent!* The characteristic odor of $HC_2H_3O_2$ indicates the presence of acetate. There are many interferences with this test, owing to the formation of gases of dominant odors, *e.g.*, HCl, SO_2, Br_2, etc.

The Ethyl Acetate Test.—To 2 drops of the unknown solution, add 2 drops of C_2H_5OH and 2 drops of concentrated H_2SO_4. The characteristic odor of $C_2H_5.C_2H_3O_2$ indicates the presence of acetate. Several anions interfere. Br^- and NO_2^- form esters which resemble $C_2H_5.C_2H_3O_2$ in odor. Other anions form gases which either dilute or mask the odor of the acetate ester.

In case of doubt, make comparison tests on (1) a drop of $NaC_2H_3O_2$ solution, and (2) a drop of water. Match the unknown against the two knowns. The test with $NaC_2H_3O_2$ is called a *control test,* and the test with water a *blank test.*

Note.—The "prepared solution" cannot be used in the above tests. It contains an excess of CO_3^{--}, and, upon acidification with H_2SO_4, excessive effervescence takes place.

The Lanthanum Nitrate-Iodine Test.—A sensitive test for $C_2H_3O_2^-$ ions is the blue color formed when I_2 is absorbed by basic lanthanum acetate. The ions of Anion Groups III and V interfere and must be previously removed. Dilute 2 drops of the unknown solution to 1 ml., make the mixture alkaline with NH_4OH, and add $Ba(NO_3)_2$-$Ca(NO_3)_2$ mixture in slight excess. Centrifuge or filter, wash, and reject the precipitate.

To the solution free from Anion Groups III and V, add 2 drops of 5 per cent $La(NO_3)_3$ solution. If a precipitate forms, dissolve it in the smallest amount of dilute HNO_3. Add 1 drop of I_2-in-KI solution, alkalize the solution with NH_4OH, and warm in a hot-water bath. A blue color indicates the presence of *acetate.*

(142) Hydroxide.—There are many sensitive tests for OH^- ions (*e.g.*, litmus, phenolphthalein, etc.), and they leave no doubt about the presence or absence of these ions in a solution. These tests, however, are of no significance, owing to the fact that many salts undergo hydrolysis, forming basic solutions; *e.g.*, $Na_2CO_3 + HOH \rightleftarrows 2Na^+ + HCO_3^- + OH^-$. There is no way of knowing from what source these OH^- ions come, the unknown or the water. The presence of hydroxides (or oxides) is best inferred from the properties of the original.

TABLE XIV.—ANALYSIS OF ANION GROUP II

In dilute solution, the anions of Group II may give no reaction with the group reagents. It is better to assume that they may be present in all unknowns except those completely insoluble in acids.

Nitrite is probably absent from solutions that are definitely acid. **(140)** To an aqueous solution of the original, add $FeSO_4 + H_2SO_4$. A brown solution indicates NO_2^-. See page 116 for interferences.	**(141)** Acidify original unknown with H_2SO_4. Odor of $HC_2H_3O_2$ indicates $C_2H_3O_2^-$. Or, add alcohol + conc. H_2SO_4. Fruity odor indicates $C_2H_3O_2^-$. See page 116 for interferences. To aqueous solution add $La(NO_3)_3$, HNO_3, I_2-in-KI, and NH_4OH. Blue color indicates $C_2H_3O_2^-$. See above for interferences.

GROUP III

(143) Presence of the Group.—The presence of Group III anions is indicated by the solubility of its Ag^+ and Ba^{++}-Ca^{++} salts in dilute HNO_3. Unfortunately, this solubility cannot be used for the purpose of separation, since certain of the anions of the group are decomposed upon acidification.

(144) Sulfite and Thiosulfate.—Place about 2 drops of the unknown solution (or a corresponding amount of a solid) in a test tube and acidify with a few drops of dilute H_2SO_4. Warm the mixture and cautiously try its odor. Note whether a precipitate of sulfur separates. The characteristic odor of SO_2, without the formation of a precipitate of sulfur, indicates the presence of *sulfite;* the odor of SO_2, accompanied by the formation of a precipitate of sulfur, indicates the presence of *thiosulfate.*

If the odor test is not decisive, repeat the procedure, passing the gas evolved into a gas trap [see (**103,** *b*)] containing acidified $KMnO_4$ solution (½ ml. of a mixture of 1 drop of $KMnO_4$ solution + 1 ml. of dilute HNO_3 + 10 ml. of water). Warm the tube in a water bath for a few minutes and, by means of a wash bottle, transfer the solution from the trap to a test tube. Add a drop of $Ba(NO_3)_2$ solution. A white precipitate of $BaSO_4$, combined with the bleaching of the $KMnO_4$ solution, indicates the presence of *sulfite.*

Notes.—1. The odor of SO_2 is not a very sensitive test, since the gas is only slowly evolved from solution, even on boiling. The explanation is found in the fact that H_2SO_3 is a fairly strong acid, with the equilibrium point in its ionization well toward the right: $SO_2 + H_2O \rightleftarrows H_2SO_3 \rightleftarrows 2H^+ + SO_3^{--}$. The reversal of this equilibrium is difficult and slow.

2. Acidified $KMnO_4$ oxidizes SO_2 to SO_4^{--}, which combines with Ba^{++} to form insoluble $BaSO_4$.

3. Commercial sulfites always contain SO_4^{--}, largely due to atmospheric oxidation.

If thiosulfate is present, dilute several drops of the solution to about 2 ml. and add $Sr(NO_3)_2$ solution until precipitation is complete. Cork the tube, appropriately labeled, and store it in the locker until the next laboratory period. Centrifuge, wash with a small portion of cold water, and make the evolution-of-SO_2 test on the precipitate, absorbing the gas evolved in dilute $KMnO_4$ solution, acidified with HNO_3. Test the solution for SO_4^{--} with $Ba(NO_3)_2$. A white precipitate indicates the presence of *sulfite.*

Notes.—1. SrS_2O_3 is soluble in water, while $SrSO_3$ is only sparingly soluble. The precipitation of $SrSO_3$ proceeds very slowly.

2. Besides $SrSO_3$, the Sr precipitate may contain a number of substances, *e.g.*, $SrSO_4$, $SrCO_3$, etc.

3. S^{--} ions, if present, must be previously removed by shaking the solution with a suspension of $CdCO_3$ and filtering. S^{--} ions would form gaseous H_2S, which would be oxidized to SO_4^{--} by the MnO_4^- ions.

(145) Carbonate.—For a large-scale test, place several drops of the original solution, or a portion of the solid about equal in size to a grain of popcorn, in a small flask or test tube fitted with a thistle tube and a delivery tube (see Fig. 13, page 92). Introduce water until the end of the tube is covered and then add dilute H_2SO_4. Heat the mixture over a low flame to gentle boiling, bubbling the gas evolved through a little $Ca(OH)_2$ solution in a test tube. A white precipitate of $CaCO_3$ is an indication of *carbonate.* The steam helps to sweep over the CO_2 and makes the test more sensitive. An excess of CO_2 may redissolve the precipitate. Reserve the solution for (**146**).

For a micro test, use 2 drops of the original solution, or a particle of the solid not larger than a small grain of rice. Place the sample in a test tube, add a fragment of metallic zinc and a few drops of dilute H_2SO_4. Promptly close the mouth of the tube with a gas trap (Fig. 14), containing a few drops of $Ca(OH)_2$ solution. If the action is too slow, place the tube in a hot-water bath. Reserve the solution for (**146**).

Note.—The Zn reacts with the H_2SO_4, forming H_2, which helps to sweep the CO_2 out of the solution.

If the unknown solution contains SO_3^{--} or $S_2O_3^{--}$, introduce 1 ml. of H_2O_2 solution before adding H_2SO_4. This will oxidize these ions to SO_4^{--} and eliminate the interference by SO_2. H_2O_2 is too weak an oxidizing agent to oxidize $C_2O_4^{--}$ to CO_2.

Notes.—1. Native carbonates (*e.g.*, dolomite and siderite) in the massive form react slowly with dilute acids. Consequently, solids should be pulverized before applying the test.

2. Vigorous boiling may spoil the test by carrying H_2SO_4 over in the spray and forming a white precipitate of $CaSO_4$. $HClO_4$ does not cause

this complication, since $Ca(ClO_4)_2$ is soluble. On the other hand, prolonged boiling with any acid may carry over enough acid in the spray to redissolve any $CaCO_3$ precipitate.

(146) Oxalate.—Use the solution reserved from **(145)**. Decant the solution from the zinc into a test tube, acidify with H_2SO_4, and add 1 drop of $KMnO_4$ solution. Use the same apparatus to detect CO_2 from $C_2O_4^{--}$ as was used to detect CO_2 from CO_3^{--}. The appearance of white $CaCO_3$ in the $Ca(OH)_2$ solution indicates the presence of *oxalate*. This inference is further indicated by bleaching the $KMnO_4$ solution.

(147) Borate.—To 1 or 2 drops of the solution add 1 or 2 drops of dilute HCl. Moisten a piece of turmeric paper with the mixture and dry it on a watch glass over a beaker of boiling water. A red color indicates *borate*. The test should be further confirmed by touching the reddened paper with a drop of dilute NaOH on a stirring rod, which gives an olive-green tint in the presence of BO_3^{---} ions.

Free H_2SO_4 interferes with the test by charring the paper upon drying. In such cases, remove the H_2SO_4 in 2 drops of the original solution by adding $BaCl_2$, centrifuging and decanting.

If Cu^{++} and Ba^{++} are absent, the flame test may be used. Two drops of the original solution are made alkaline with NaOH and evaporated to dryness in a crucible one-quarter full of clean sand. Instead of the original solution, 1 ml. of the "prepared solution" may be used, omitting the addition of NaOH. Add 2 drops of ethyl alcohol and 2 drops of concentrated H_2SO_4 and heat the crucible on a triangle above a Bunsen burner until the alcohol takes fire. A flame edged with green indicates the presence of borate.

Notes.—1. Cu^{++} and Ba^{++} interfere by coloring the flame green.

2. Borate solutions must be made alkaline before evaporation, since H_3BO_3 is volatile in steam.

3. Chlorides tend to form ethyl chloride, C_2H_5Cl, which tinges the flame green.

(148) Arsenate and Arsenite.—The detection of these ions is based mainly upon the reactions in Cation Group II.

Pentavalent arsenic is assumed to be present in solution as AsO_4^{---}. This anion is indicated by the following reactions:

(1) The difficult precipitation of the sulfide, (2) the oxidation of I^- to I_2 in acid solution, (3) the formation of chocolate-brown Ag_3AsO_4 without the intervention of an oxidizing agent, and (4), most significant of all, the presence of oxidizing constituents in the solution.

Trivalent arsenic is assumed to be present in acid media as As^{+++}, and in neutral and alkaline media as AsO_3^{---} or AsO_2^-. Trivalent arsenic differs from pentavalent arsenic in the following respects: (1) Its sulfide is easily precipitated in acid solution; (2) it decolorizes I_2 solutions in neutral medium; (3) it forms yellow Ag_3AsO_3, soluble in strong acids and in NH_4OH; (4) if the solution contains strong reducing agents, As must be present in the reduced form.

(149) **Phosphate.**—If AsO_4^{---} may be present—*i.e.*, if arsenic was found in cation analysis—evaporate 2 drops of the solution to dryness and take up the residue in 5 ml. of concentrated HCl. Place this solution in a small Erlenmeyer flask, heat nearly to boiling, and saturate thoroughly with H_2S. Test for completeness of the reaction before proceeding with the next step. Decant the solution from the precipitate and add 1 ml. of concentrated HNO_3. Evaporate to a paste (hood) and dissolve in a few drops of dilute HNO_3.

Acidify the As-free solution (1 or 2 drops, if the original is used) with concentrated HNO_3 and add a few drops of the $(NH_4)_2MoO_4$ reagent. Heat in the water bath for several minutes. A yellow precipitate of $(NH_4)_3PO_4.12MoO_3$ indicates the presence of phosphate.

Note.—AsO_4^{---} ions give with $(NH_4)_2MoO_4$ reagent a yellow precipitate similar to the phosphate precipitate.

(150) **Chromate and Dichromate.**—The detection of these ions is based upon reactions met during cation analysis. A change in color from orange to milky green during the H_2S precipitation of Group II, followed by the detection of Cr^{+++} in Group III, is sufficient indication of their presence.

In case of doubt, take 2 drops of the solution of the original unknown, add 2 drops of dilute H_2SO_4, 0.5 ml. of ether, and 1 or 2 drops of H_2O_2 solution. Shake or centrifuge promptly.

A blue color in the ether layer indicates the presence of *chromate* or *dichromate*. [See (**48**, *d*), page 46.] If the original solution is neutral or basic, the ion may be assumed to be CrO_4^{--}; if the solution is acid, $Cr_2O_7^{--}$.

TABLE XV.—ANALYSIS OF ANION GROUP III

(**143**) In the absence of Anion Group I, Group III is indicated by the formation of a precipitate with $AgNO_3$; and in the absence of Anion Group V by the formation of a precipitate with $Ba(NO_3)_2$. If both of these interfering groups are present, it is better to make specific tests for each member of Group III.

(**144**) Acidify original unknown with H_2SO_4, warm, and absorb gases evolved in $KMnO_4 + Ba(NO_3)_2 + HNO_3$. Bleaching of $KMnO_4$ and formation of white $BaSO_4$ indicates SO_3^{--} or $S_2O_3^{--}$. An S precipitate indicates $S_2O_3^{--}$. In the presence of $S_2O_3^{--}$ test for SO_3^{--} by $Sr(NO_3)_2$.

(**145**) If SO_3^{--} or $S_2O_3^{--}$ is present, add H_2O_2 and H_2SO_4 and absorb any CO_2 evolved in $Ca(OH)_2$. White $CaCO_3$ indicates CO_3^{--}. Reserve solution for (**146**).

(**146**) To solution reserved from (**145**) add $KMnO_4$. Absorb any CO_2 evolved in $Ca(OH)_2$. Bleaching of $KMnO_4$ and formation of white $CaCO_3$ indicate $C_2O_4^{--}$.

(**147**) Moisten turmeric paper with HCl solution of unknown and dry over water bath. Red color indicates BO_3^{---}. Confirm by adding NaOH, giving green color.

Flame test: Remove Cu^{++} and Ba^{++} by Na_2CO_3, evaporate filtrate. Mix residue with alcohol + conc. H_2SO_4, ignite. Flame edged with green indicates BO_3^{---}.

(**148**) If As has been found in neutral or alkaline unknown, assume presence of AsO_3^{---} or AsO_4^{---}. Distinguish between these by reactions with I_2, H_2S, etc.

(**149**) To an HNO_3 solution of the unknown, add $(NH_4)_2MoO_4$ reagent and warm. Yellow precipitate, $(NH_4)_3PO_4.12MoO_3$, indicates PO_4^{---} (in the absence of AsO_4^{---} or AsO_3^{---}). Previous to this test, remove As ions by dissolving unknown in conc. HCl and saturating with H_2S.

(**150**) If the color of the original was yellow or orange, changing to green upon treatment with H_2S + HCl, and if Cr^{+++} was found in Cation Group III, CrO_4^{--} or $Cr_2O_7^{--}$ is indicated.

GROUP IV

(151) Presence of the Group.—Since the ions of this group give no reaction with the group reagents, tests for each of them must be made in all cases, except when the possibility of their presence is excluded by solubility considerations or by reducing constituents.

(152) Nitrate.—The best procedure is determined by the presence or absence of interfering ions.

(*a*) *Nitrite Is Present.*—If NO_2^- has been found, the presence of NO_3^- may be assumed without making a test, since nitrates are constant impurities in nitrites.

(*b*) *Brown-ring Test.*—There are many interferences with this test: I^-, CrO_4^{--} or $Cr_2O_7^{--}$, ClO_3^-, $Fe(CN)_6^{----}$, $Fe(CN)_6^{---}$, Pb^{++}, Ba^{++}, Sr^{++}, and colored ions in general. In such cases, use the "evolution-of-NH_3" test below.

Place a drop of the solution in a test tube and acidify with dilute H_2SO_4, in order to avoid effervescence when brought into contact with concentrated H_2SO_4. Add 1 drop of $FeSO_4$ and dilute to about 0.5 ml. Then, by means of a pipette, introduce several drops of concentrated H_2SO_4 beneath the solution. A brown ring at the junction of the two layers indicates the presence of *nitrate.*

(*c*) *Evolution-of-NH_3 Test.*—Place a drop of the solution in a crucible or small beaker, add several drops of concentrated NaOH solution, and warm gently until all NH_4^+ ions are expelled as NH_3. Then add to the warm solution a little Zn dust and promptly cover with a watch glass carrying on its lower surface a piece of moist red litmus paper. The change in color from red to blue indicates *nitrate.*

(153) Chlorate.—The ions of Anion Group I interfere with the detection of ClO_3^-. Hence, if Group I ions were found to be present in **(132)**, remove them according to *A* below; if they are absent, proceed to *B*.

A. Removal of Group I Anions.—Acidify 1 or 2 drops of the solution with 2 or 3 drops of dilute H_2SO_4 and add $AgNO_3$ solution dropwise until precipitation is complete. Centrifuge or filter, and wash the precipitate with a few drops of cold water. Reserve the combined decantates for *B*.

B. Detection of Chlorate.—Use 2 or 3 drops of the original solution (if free from the anions of Group I) or the solution from *A* above from which Group I ions have been removed. If the solution is not already acid, acidify with 2 or 3 drops of dilute H_2SO_4. Place the solution in a test tube and add a piece of metallic zinc about the size of a grain of rice. Heat the mixture in a water bath for several minutes. Decant or filter the solution and test it for Cl^- by means of $AgNO_3$ solution. A precipitate of AgCl indicates the presence of *chlorate* in the mixture. If the test for ClO_4^- is to be made, reserve the mixture for (**154**).

(**154**) **Perchlorate.**—This test is made on the mixture reserved from (**153**).

Centrifuge or filter the mixture and evaporate the solution to bare dryness in a small evaporating dish or a crucible over a micro flame. Add 1 drop each of Na_2CO_3 and 50 per cent $Mn(NO_3)_2$ and ignite to almost red heat. Cool and extract with 1 ml. of NH_4OH. Acidify the extract with HNO_3 solution. A precipitate of AgCl indicates the presence of *perchlorate* in the original.

Table XVI.—Analysis of Group IV

(**151**) Tests for the members of this group should be made on all unknowns except those in which their absence is positively indicated by solubility considerations or the presence of reducing constituents.	
(**152,** *b*) Acidify a portion of the original solution with H_2SO_4, add $FeSO_4$, and introduce conc. H_2SO_4 below the mixture. A brown ring indicates NO_3^- (in the absence of interfering ions). (**152,** *c*) Warm a portion of the original with NaOH to remove NH_4^+. Add Zn dust and warm. Vapor turning red litmus paper blue indicates NO_3^- (in absence of NO_2^-).	(**153**) If Group I anions are present, add $AgNO_3$ + dilute H_2SO_4. Centrifuge, reject precipitate. Warm solution containing excess H_2SO_4 with Zn, and decant. To solution add $AgNO_3$. White precipitate of AgCl indicates ClO_3^-. Centrifuge and reserve solution for (**154**).
(**155**) Purple solution, decolorized by H_2S + HCl, followed by detection of Mn^{++} in Group III, indicate MnO_4^-.	(**154**) Evaporate solution from (**153**), add Na_2CO_3, $Mn(NO_3)_2$, and ignite. Extract residue with NH_4OH, acidify extract with HNO_3, and add $AgNO_3$. White AgCl indicates ClO_4^-.

(155) Permanganate.—The permanganate ion, MnO_4^-, is detected during the analysis for cations. A red-to-violet solution, decolorized during the H_2S precipitation in **(31)**, followed by the detection of Mn^{++} in **(60)**, are sufficient indications of the presence of *permanganate.*

GROUP V

(156) Test for the Group.—Dilute 1 or 2 drops of the unknown solution, acidify with HNO_3, and add 1 drop of $Ba(NO_3)_2$-$Ca(NO_3)_2$ mixture. A white precipitate indicates the presence of Group V anions. If SiF_6^{--} may be present, proceed to **(157)**; if SiF_6^{--} is known to be absent, proceed to **(158)**.

If the substance is a solid, insoluble in acids, direct tests for F^- and SO_4^{--} may be made according to **(158)** and **(159)**.

(157) Fluosilicate.—Place 2 or 3 drops of the solution in a test tube, dilute to 1 ml. with water, and add an equal volume of 95 per cent alcohol. Add KCl solution dropwise until precipitation is complete. Centrifuge or filter, wash, and reserve the solution for **(158)**. The precipitate contains any SiF_6^{--} as K_2SiF_6.

Confirm the presence of SiF_6^{--} by adding to the moist residue 1 or 2 drops of concentrated H_2SO_4. Close the mouth of the tube with a slotted cork carrying a short piece of glass tubing that has just been dipped in water. Warm the tube in the water bath for several minutes. A turbidity in the drop of water indicates the presence of *fluosilicate.*

Note.—The H_2SO_4 converts the SiF_6^{--} into H_2SiF_6, which decomposes upon warming into $2HF + SiF_4$. The latter reacts with the drop of water on the tubing, forming a precipitate of $Si(OH)_4$: $3SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 2H_2SiF_6$.

(158) Fluoride.—Follow *A* or *B*.

A. The Unknown Is a Solution.—If the solution is a filtrate from **(157)**, evaporate it to a small volume in a casserole over a small flame, or better, over a water bath. The alcohol will probably take fire and burn harmlessly. Take up the residue in a little water and proceed by the next paragraph. If the solution is part of the original unknown, dilute 1 or 2 drops to about 1 ml.

Acidify the solution with HNO_3 and add $Ca(NO_3)_2$ solution dropwise until precipitation is complete. A white gelatinous precipitate is CaF_2, and a white crystalline precipitate is $CaSO_4$. Centrifuge, decant, and reserve the solution for **(159)**. Transfer the precipitate to a watch glass and dry it over a beaker of boiling water. Proceed to *B*.

Notes.—1. Precipitated CaF_2 is gelatinous and filters slowly.

2. The presence of $CaSO_4$ in the precipitate does not interfere with the subsequent test for F^-.

B. The Substance Is a Solid.—Mix a little of the solid with an equal volume of SiO_2 and place the mixture in a dry test tube. Add a drop of concentrated H_2SO_4 and introduce into the tube a slotted cork carrying a small piece of glass tubing which has just been dipped in water. Heat the tube in the water bath for

TABLE XVII.—ANALYSIS OF GROUP V

<table>
<tr><td colspan="3"><i>A. The Unknown Is a Solution.</i>—(156) Acidify a portion with HNO_3 and add $Ba(NO_3)_2$-$Ca(NO_3)_2$. A white precipitate indicates Group V. If SiF_6^{--} may be present, proceed to (157); if it is known to be absent, proceed to (158).</td></tr>
<tr><td colspan="3">(157) To unknown solution add KCl and alcohol. Centrifuge, wash precipitate with 50 per cent alcohol.</td></tr>
<tr><td rowspan="2">Precipitate: White K_2SiF_6. Confirm by adding conc. H_2SO_4 and heating. Absorb gas evolved in drop of water. Turbidity of $Si(OH)_4$ indicates SiF_6^{--}.</td><td colspan="2">Filtrate: F^-, SO_4^{--}, alcohol, etc. Evaporate, dilute.
(158) Add $Ca(NO_3)_2$, centrifuge or filter, wash precipitate.</td></tr>
<tr><td>Precipitate: CaF_2, $CaSO_4$. Proceed to <i>B</i>.</td><td>(159) Filtrate: Saturated $CaSO_4$. Add $Ba(NO_3)_2$. White precipitate of $BaSO_4$ indicates SO_4^{--}.</td></tr>
<tr><td colspan="3"><i>B. The Unknown Is a Solid,</i> insoluble in dilute acids.</td></tr>
<tr><td colspan="2">(158) Mix powdered substance with SiO_2 and conc. H_2SO_4. Heat and absorb gas evolved in a drop of water. Turbidity of $Si(OH)_4$ indicates F^-.</td><td>(159) Mix powdered substance with charcoal and Na_2CO_3 and heat to redness. Cool, add HCl, and test evolved gas with $Pb(C_2H_3O_2)_2$ paper. Brown stain indicates SO_4^{--}.</td></tr>
</table>

several minutes. A turbidity in the drop of water indicates the presence of *fluoride.*

(159) Sulfate.—Proceed according to *A* or *B*.

A. The Unknown Is a Solution.—To the solution, free from SiF_6^{--} and F^-, add 1 drop of $Ba(NO_3)_2$ or $BaCl_2$ solution. A white precipitate, insoluble in water and in strong acids, indicates the presence of *sulfate.*

Note.—Solutions containing high concentrations of NO_3^- ions may give a precipitate of $Ba(NO_3)_2$ when the Ba^{++} reagent is added. This precipitate, however, dissolves easily in warm water.

B. The Unknown Is a Solid.—Grind a pinch of the substance very fine in a mortar with three times its volume of charcoal and three times its volume of powdered Na_2CO_3. Heat the mixture to low redness in a crucible for several minutes. Let the crucible cool, place it in a small beaker, and add to the residue in the crucible several drops of dilute HCl. Cover the beaker promptly with a filter paper moistened with 1 drop of $Pb(C_2H_3O_2)_2$ solution. A black stain, due to PbS, indicates the presence of sulfide, formed by the reduction of *sulfate.*

GROUP VI

(160) Silicate and Silica.—Proceed according to *A* or *B*.

A. The Unknown Is an Alkaline Solution.—Place 2 drops of the solution on a watch glass, acidify with about 2 drops of dilute HCl, and evaporate to dryness over a beaker of boiling water. Wash the residue into a test tube with a small amount of water. If the residue dissolves completely, SiO_3^{--} ions are absent. Test the residue for SiO_2 by the drop-of-water and metaphosphate-bead tests, below.

B. The Unknown Is a Solid.—If acid-soluble constituents have not already been removed, pulverize thoroughly in a mortar and extract with dilute acids until an acid-insoluble residue remains. Use small portions of the residue for the following tests.

Mix a pinch of the *finely* divided material with an equal volume of CaF_2 (precipitated) and make a drop-of-water test as in (**158,** *B*). A turbidity indicates the presence of *silica.*

Using the remainder of the residue, try its solubility in Na_2CO_3 [see (**116,** *b*)] and $NaPO_3$ beads [see (**116,** *c*)]. If the material gives a clear Na_2CO_3 bead and an opaque $NaPO_3$ bead, *silica* is indicated.

Notes.—1. The principal interference with the drop-of-water test is fluosilicate.

2. A number of substances insoluble in acids give opaque beads with Na_2CO_3 and $NaPO_3$. They do not respond to the drop-of-water test and are eliminated in that way.

TABLE XVIII.—ANALYSIS OF ANION GROUP VI

(**160**) *A*. If unknown is a strongly alkaline solution, acidify with HCl and evaporate. Test residue by *B*.

B. If unknown is a solid, pulverize and extract with warm HCl. Mix portion of residue with CaF_2, add conc. H_2SO_4, and make drop-of-water test for SiF_4. A turbidity indicates SiO_2 or SiO_3^{--}. Use remainder of residue for bead tests with Na_2CO_3 and $NaPO_3$. A clear Na_2CO_3 bead and an opaque $NaPO_3$ bead indicate SiO_2.

Exercises

1. List the anions too volatile to be found in strongly acid solutions open to the air.
2. List the acids too unstable to be found in strongly acid solutions.
3. A solid insoluble in water but soluble in HNO_3 contains Pb^{++}. What anions may it contain?
4. A strongly acid solution contains Ag^+ and Ba^{++}. What anions may be found?
5. What anions may be present in a neutral solution containing Cd^{++} and Sr^{++}?
6. An unknown insoluble in water but soluble in dilute HCl contains Mn^{++} and Zn^{++}. What anions should be tested for? If the unknown dissolves in HCl without effervescence, which of these anions could not be present?
7. An acidic solution containing Cu^{++} as its only metallic ion can be neutralized without precipitate formation. What anions may be present?
8. What cations could be present in a neutral solution containing PO_4^{---}? CrO_4^{--}?
9. A neutral solution is found to contain both Pb^{++} and SO_4^{--}. How is this possible when $PbSO_4$ is insoluble in water?
10. Name neutral salt solutions that will dissolve the following: (*a*) AgCl, (*b*) NiC_2O_4, (*c*) $Cu(OH)_2$, and (*d*) $Mg(OH)_2$.
11. A white powder, insoluble in water, dissolves in dilute HCl without effervescence. Ca^{++} is the only cation found in the solution. List the possible calcium compounds.

12. A red ferric compound is insoluble in water but dissolves in HCl to an amber solution. Tests for all the anions forming acid-soluble compounds with Fe^{+++} give negative results. What is the substance?

13. Name two salts that you would not expect to be transposed by boiling Na_2CO_3 solution.

14. What ions are never present in solids wholly insoluble in water?

15. Why should $S_2O_3^{--}$ be removed before testing for the presence of anion Group I?

16. Why should commercial Na_2CO_3 contain small amounts of NaCl?

17. The presence of Cation Groups I, II, III, and IV (sometimes called the "heavy metals") interferes with the tests for which group of anions?

18. Will boiling with concentrated Na_2CO_3 solution precipitate As from an unknown solution? In an alkaline solution, does As act as a metal or a non-metal?

19. Cation analysis of the solution of a simple salt shows the presence of K^+ and either As^{+++} or As^{+++++}. The solution gives a yellow precipitate with $AgNO_3$ solution. Identify the salt.

20. A yellow mercury compound is insoluble in water but soluble in acids. The HNO_3 solution of this substance gives negative tests for all anions except NO_3^-. What is the substance?

21. What carbonates react with least vigor with acids?

22. How could you distinguish between pulverized CaF_2 and fine SiO_2 by the use of the bead test?

23. How would you proceed to test for SCN^- in a solution containing Co^{++}?

24. Cation analysis of an unknown solution indicates Pb^{++} and NH_4^+. $C_2H_3O_2^-$ is indicated as present as an anion by the H_2SO_4 test. What other anions should be tested for?

25. Name a yellow-colored anion that would interfere with the brown-ring test for NO_3^-. How would you test for NO_3^- in such a case?

26. An unknown is in the form of an amber-colored solution containing a brown sediment. The solution does not give a yellow color to methyl violet. The only ions found in the analysis are Fe^{+++} and SO_4^{--}. Interpret.

27. A white powder effervesces violently when concentrated H_2SO_4 is added. It dissolves readily in water, giving a solution which forms a brown precipitate with $AgNO_3$. Analysis gives a strong test for Na^+ and a weak test for CO_3^{--}, all other tests being negative. What is the powder?

PART IV

SYSTEMATIC ANALYSIS

Note.—The following outline for the systematic analysis of unknown substances is not exhaustive, giving only methods for detecting the commoner elements in rather simple modes of combination. For a thorough treatment consult advanced textbooks.

In carrying out a complete analysis of an unknown substance, the student should take advantage of the information afforded by such properties as color, general appearance, solubility, behavior on solution, etc. If the material is a natural or commercial product, he should keep in mind the probable composition, should know what impurities are most likely, and should not waste any time testing for ions that common sense would indicate to be absent. As illustrative of this last point, a commercial alloy would not be likely to contain strontium or potassium, nor would an ore contain acetate or oxalate.

Proper attention should be paid to the relative amounts of the various ingredients found. If only a trace of an ion is present, it should be reported as such. Due consideration should be given to the intensity of the test, since certain tests are much more sensitive than others. For example, a trace of Fe^{+++} gives a strong coloration with NH_4SCN solution.

REMOVAL OF ORGANIC MATTER

(161) Organic matter, if present, must be removed before carrying out the analysis for metallic ions. Hydroxy-organic compounds, like tartrates, citrates, sugars, etc., are particularly objectionable, since they prevent the precipitation of $Al(OH)_3$ and $Cr(OH)_3$ in Group III.

Test.—Heat a small portion of the solid substance (obtained in the case of solutions by evaporation) in a porcelain crucible or on a crucible lid. A charring effect and an odor like that of burned sugar indicate the presence of organic matter.

Removal.—If organic matter is present, place about 5 ml. of a solution or 0.5 gram of a solid in a small flask, add 5 ml. of concentrated HNO_3, and heat as long as brown fumes are given off. If the solution remains brown, add more HNO_3 and heat again. This may be repeated as many times as necessary. Concentrated H_2SO_4 is sometimes added along with the HNO_3. When oxidation is complete, cool, dilute the solution, centrifuge or filter (if necessary), and wash any precipitate. Analyze the solution for cations by (**18**) to (**89**). Test any residue for the cations forming insoluble sulfates by fusing a portion with Na_2CO_3 (page 135), for Al_2O_3 and Fe_2O_3 by fusing another portion with $KHSO_4$ (page 134), and for SiO_2, using a third portion, by (**160**). As usual, the test for NH_4^+ must be made on a portion of the original substance.

DISSOLVING THE SUBSTANCE

(162) Solids, Not Metals or Alloys.—The material, if not a metal or an alloy [see (**163**)], should be ground as finely as possible in a mortar and then treated with the following solvents, both hot and cold, in the order given:

1. Water.
2. HNO_3, dilute and concentrated.
3. HCl, dilute and concentrated.
4. Aqua regia.

In case any one of the solvents effects a partial solution, the treatment should be continued as long as there is any action. The residue is then filtered off and subjected to the action of the other solvents or otherwise identified.

(163) Metals and Alloys.—There are certain natural limitations to the composition of alloys. With the exception of magnesium, the metals of Cation Groups IV and V are very seldom found in alloys that are stable toward water or ordinary (moist) air. On the other hand, metals and alloys may contain certain non-metals, the most important of which are C, Si, and P and are found in most iron alloys. Provisions for the detection of these elements are given in the procedure below.

Dissolving the Material.—Use a small sample for analysis, not more than 0.1 gram. Preferably it should be in the form of filings, turnings, or pellets. Place the sample in a test tube and add about 2 ml. of dilute HNO_3. Heat in the water bath as long as there is any solvent action. More acid may be added to replace that used up in the action.

The formation of a white precipitate (usually metastannic acid, $SnO_2.xH_2O$, or antimony oxide, Sb_2O_4) indicates that HNO_3 is not the proper solvent. In such a case add an equal volume of concentrated HCl, making aqua regia the solvent.

Note.—The adding of indefinite amounts of concentrated acids in order to effect a speedy solution of an alloy is discouraged. As will be seen below, excess of acid must be boiled out; moreover, in some cases, dilute acids are actually better solvents than concentrated acids.

If HNO_3 appears to have little effect on the substance, pour it off, add 2 ml. of dilute HCl, and heat in the water bath. Certain metals and alloys insoluble in HNO_3 are soluble in HCl, *e.g.*, Al, Fe, Cr, and their alloys.

Notes.—1. When metals otherwise active are inert toward HNO_3 and certain other oxidizing agents, they are said to be in the "passive state," a condition little understood. (See advanced textbooks.)

2. HCl, like HNO_3, has certain advantages and disadvantages as a solvent for alloys. Although it reacts rapidly with some metals, HCl, as a rule, is slower than HNO_3 and is practically without action on metals occurring below hydrogen in the Electromotive Series. (See Appendix, page 140.) Furthermore, As and Sb, if present in small amounts, may be completely lost as arsine, AsH_3, and stibine, SbH_3, owing to the reducing action of nascent hydrogen. The proper solvent for an unknown alloy must be determined experimentally.

If a metallic-looking residue remains, insoluble in HNO_3 and HCl taken separately, add 2 ml. of dilute HCl and 1 ml. of dilute HNO_3 and warm until action is complete.

Combine all the solutions obtained in the preceding paragraphs, reserving any insoluble residue for the tests for C and Si. If a precipitate is formed when the HNO_3 and HCl (or aqua regia) solutions are mixed, Cation Group I is present. Filter and wash the precipitate and analyze it by (**19**) and (**20**). Analyze the filtrate for the ions of Groups II, III, and IV and Mg^{++} by (**30**) and subsequent procedures, reserving a small portion for the P test below.

Phosphorus.—Test a small portion of the filtrate from the above procedure for PO_4^{---} by (**149**), page 121. If PO_4^{---} is found, the presence of P in the alloy is indicated.

The residue insoluble in acids probably consists of such substances as C, SiO_2, SiC, etc. Dry by heating on a watch glass over a beaker of boiling water, and test portions of it as follows:

Carbon.—Place about 0.5 gram of dry $KClO_3$ in a hard-glass test tube and heat until the salt is just melted. Drop into the melt a minute (Be careful not to use too much!) portion of the residue. Inflammation, with a harmless explosion, indicates the presence of carbon.

Silicon.—Test another portion of the residue for SiO_2 by a metaphosphate bead. [See (**116,** *c*), page 102.]

(164) Ores and Insoluble Salts.—The material is ground to a very fine powder in a mortar, and the following solvents are tried in order:

Water.—Place about 0.1 gram of the powdered substance in a test tube and add about 2 ml. of water and heat in a water bath. If the material dissolves completely, analyze the solution for cations and anions according to the procedures of Parts II and III.

Nitric Acid.—If the substance is not soluble in water, add, without filtering, 1 ml. of concentrated HNO_3. Warm as long as brown fumes are given off. If the action of HNO_3 appears incomplete, allow the heavy precipitate to settle and decant the solution, and repeat the HNO_3 treatment on the residue. Centrifuge or filter, and reserve all solutions for later analysis.

Aqua Regia.—If the residue from the HNO_3 treatment seems to consist of something more than SiO_2, add 2 ml. of dilute HCl and 1 ml. of dilute HNO_3 and warm. When the reaction is complete, dilute and filter, reserving the residue for the next paragraph. Combine all the filtrates obtained up to this point. If a precipitate forms upon mixing the HNO_3 solution with the aqua regia solution, Cation Group I is present. Centrifuge or filter, wash the precipitate, treat the residue by (**19**) and (**20**), and treat the filtrate[1] by (**30**) and the subsequent procedures.

Examine the residue closely. If the substance is an ore, the residue may be nothing but sand discolored by traces of the undissolved substance. Test it by a metaphosphate bead. [See (**116,** *c*), page 102.] If the residue is gummy and tends to float in the hot HNO_3 or aqua regia solution, it may be sulfur. Test it by (**135,** *C*). If the residue seems to have been practically unaffected by the acid treatment, especially if the acid solution appears to contain very little dissolved material, a substance insoluble in acids is indicated. Proceed to the next paragraph.

---

[1] In case of doubt as to whether the solution contains any metallic ions, evaporate a small portion on a watch glass over a beaker of boiling water. If no residue remains, discard the solution.

Fusion with Potassium Hydrogen Sulfate.—Mix the substance insoluble in acids with ten times its weight of solid potassium hydrogen sulfate (also called potassium bisulfate), $KHSO_4$, and grind them together in a clean mortar. Transfer the mixture to a porcelain crucible and heat over a Meker burner or a blast lamp, at first gently until frothing has ceased, and then at maximum heat until a clear melt is obtained. Allow the crucible to cool, place it on its side in a beaker, and cover it with water containing 4 ml. of dilute HNO_3. As soon as the solid is detached from the crucible, remove the latter. By means of the rounded end of a stirring rod, carefully disintegrate any solids in the mixture. Boil gently for 5 min. and filter or decant. Wash the residue[1] and reserve it for the next paragraph. Analyze the filtrate for cations according to (**18**) to (**89**), omitting (**88**).

Notes.—1. The residue insoluble in acids may contain S, AgCl, $PbSO_4$, $PbCrO_4$ (fused), SnO_2 (native), Al_2O_3 (ignited), Cr_2O_3 (ignited), $Fe(CrO_2)_2$, $BaSO_4$, $SrSO_4$, $CaSO_4$, CaF_2, SiO_2 and many silicates. Ag^+ is present as AgCl, since the previous aqua regia treatment converts AgBr, AgI, etc., into AgCl.

2. Upon heating, $KHSO_4$ first melts and at about 300° decomposes, giving potassium pyrosulfate, thus: $2KHSO_4 \rightarrow K_2S_2O_7 + H_2O$. At still higher temperatures further decomposition takes place, giving the normal sulfate and SO_3: $K_2S_2O_7 \rightarrow K_2SO_4 + SO_3$. The solvent action of $K_2S_2O_7$ is similar to that of H_2SO_4, but more intense, since it is used at higher temperatures.

3. Fusion with $KHSO_4$ brings about the following changes: S is volatilized or oxidized; AgCl is converted into Ag_2SO_4, $PbCrO_4$ into $PbSO_4$ and $Cr_2(SO_4)_3$, Al_2O_3 into $Al_2(SO_4)_3$, Cr_2O_3 into $Cr_2(SO_4)_3$, CaF_2 into $CaSO_4$ and KF, and silicates are "opened up" so that their cations may be brought into solution by acids. The filtrate contains the cations which form soluble sulfates; and the residue contains the insoluble sulfates $PbSO_4$, $BaSO_4$, $SrSO_4$, and $CaSO_4$, along with other insoluble substances like SnO_2 and SiO_2.

---

[1] If the decomposition of the insoluble substance by the $K_2S_2O_7$ seems incomplete, repeat the fusion with a fresh charge of $KHSO_4$.

Fusion by Sodium Carbonate.—Mix the residue not decomposed by the pyrosulfate fusion with 5 grams of anhydrous Na_2CO_3 and 1 gram of KNO_3 and heat in a porcelain[1] crucible over a Meker burner or blast lamp until the mixture ceases to effervesce or show any signs of action. If the reaction seems incomplete, more Na_2CO_3 should be added and the mixture again heated. After the reaction is complete, cool, place the crucible in a beaker, cover with water, and boil for some time. If some of the material adheres to the crucible, remove the latter from the beaker and carefully loosen the melt by means of a stirring rod. Break up all large particles with a stirring rod, filter, and wash the residue. Reject the filtrate. Add to the residue dilute HCl, dilute, and warm as long as any of the substance seems to dissolve. Filter, wash the precipitate, and analyze the filtrate for cations by (**30**) to (**85**). Besides Pb^{++}, Ba^{++}, Sr^{++}, and Ca^{++}, other cations not completely removed by the pyrosulfate fusion may be detected.

The residue contains SnO_2 and probably some undecomposed silicates, sulfates, etc. If SnO_2 may be present, treat the residue according to the next paragraph.

Notes.—1. The KNO_3 is added to the fusion mixture to help dissolve oxidizable substances like Cr_2O_3.

2. The filtrate from the Na_2CO_3 fusion may contain, besides Na_2SO_4, Na_2SiO_3, and Na_2CO_3, such soluble materials as Na_3AsO_4 and Na_2CrO_4. If As and Cr have not been detected already, and if they might be present in the original, this solution should be analyzed for AsO_4^{---} and CrO_4^{--} in the regular way.

Native Stannic Oxide (Cassiterite).—Mix a portion of the residue from the preceding paragraph with six times its weight of Na_2CO_3 and S (equal parts mixed together), cover the crucible with a crucible lid, and heat over a small flame until the excess of sulfur has distilled off and burned. The operation requires about 20 min. Allow the crucible to cool and then treat its contents with hot water. Filter out any undissolved residue and analyze the filtrate for Sn^{++++} by (**42**), page 42.

---

[1] A platinum crucible, if available, is much more satisfactory, provided that easily reducible metals like Ag, Pb, Bi, As, Sb, and Sn are absent. These metals form easily fusible alloys with Pt, with the result that the crucible is melted out and ruined. The chief difficulty in using porcelain is that this material is attacked by the alkaline melt, and certain amounts of Al and SiO_2 are introduced into the melt.

Note.—The reaction involved in this procedure is $2SnO_2 + 2Na_2CO_3 + 9S \rightarrow 3SO_2 + 2Na_2SnS_3 + 2CO_2$. Iron and other metals that might be present remain in the residue as sulfides.

TABLE XIX.—SOLUTION OF SOLIDS INSOLUBLE IN ACIDS

<table>
<tr><td colspan="4">Residue: $\underline{S}$, $\underline{AgCl}$, $\underline{PbSO_4}$, fused $\underline{PbCrO_4}$, native $\underline{SnO_2}$, ignited $\underline{Al_2O_3}$ and $\underline{Cr_2O_3}$, $\underline{Fe(CrO_2)_2}$, $\underline{BaSO_4}$, $\underline{SrSO_4}$, $\underline{CaSO_4}$, $\underline{CaF_2}$, $\underline{SiO_2}$, and many silicates. Add $KHSO_4$, grind in a mortar, fuse in a porcelain crucible, cool, and extract with hot dilute HNO_3.</td></tr>
<tr><td rowspan="3">Solution: All cations except Pb^{++}, Ba^{++}, Sr^{++}. Analyze solution by (18) to (89).</td><td colspan="3">Residue: $\underline{PbSO_4}$, $\underline{BaSO_4}$, $\underline{SrSO_4}$, $\underline{CaSO_4}$, $\underline{SnO_2}$, $\underline{SiO_2}$ (and some of the acid-insoluble residue not decomposed in the pyrosulfate fusion). Mix with Na_2CO_3 and KNO_3 and fuse in a porcelain crucible. Disintegrate residue, extract with hot water. Filter, wash precipitate.</td></tr>
<tr><td rowspan="2">Filtrate: Na_2SO_4, Na_2SiO_3, Na_2CO_3. Discard.</td><td colspan="2">Residue: $\underline{PbCO_3}$, $\underline{BaCO_3}$, $\underline{SrCO_3}$, $\underline{CaCO_3}$, (and some unchanged sulfates and silicates). Extract with hot dilute HNO_3. Wash residue.</td></tr>
<tr><td>Solution: Pb^{++}, Ba^{++}, Sr^{++}, Ca^{++}. Analyze by (30) to (85).</td><td>Residue: SnO_2 and undecomposed sulfates, silicates, etc. Make special test for native SnO_2.</td></tr>
</table>

APPENDIX

THE LABORATORY RECORD

A complete record of all laboratory exercises should be kept in one of the official notebooks prescribed for the course.

Preliminary Experiments.—The notes on the preliminary experiments should contain in outline form a record of all the processes carried out, along with a clear statement of the results obtained and the inferences drawn. The style should be concise, rather than narrative and descriptive. As far as possible, the device of "labeled equations" should be used. By way of example, specimen notes on the preliminary experiments on the silver ion, Ag^+, are given below.

SPECIMEN NOTES

(16) Silver, Ag^+. March 10, 1940.

(*a*) *Insolubility of Silver Chloride in Water.*

$$Ag^+ + Cl^- \rightarrow \underset{\substack{\text{Silver chloride,}\\ \text{white, curdy,}\\ \text{washed by}\\ \text{decantation}}}{\underline{AgCl}}$$

AgCl is insoluble in water, because washings with hot water gave no brown precipitate with H_2S.

(*b*) *The Silver-Ammonia Complex Ion.*

$$\underline{AgCl} + 2NH_3 \text{ (in } NH_4OH) \rightarrow \underset{\substack{\text{Silver-ammonia}\\ \text{complex ion}}}{Ag(NH_3)_2^+} + Cl^-$$

$$Ag(NH_3)_2^+ + Cl^- + 2H^+ \rightarrow \underline{AgCl} + 2NH_4^+$$

It should be noted that equations alone are not sufficient. Descriptive and interpretative statements must be included when called for in the laboratory directions.

Underscore all precipitates; gases formed should be indicated by overscoring or by arrows pointed upwards. Solutions are designated by omitting these signs. See above specimen notes.

The headings of the experiments should always be included in the notes, since they indicate not only the subject but frequently the inferences reached in the experiments.

Equations should show only the substances which are actually used or formed in the reaction. If a reaction takes place "in the presence of" a substance, indicate the latter by placing its formula above the arrow, thus:

$$Cu^{++} + H_2S \xrightarrow{\text{Dil. HCl}} \underline{CuS} + 2H^+$$

Do not write an equation every time two substances are mixed. For example, $Cu(NO_3)_2$ solution and dilute HCl may be assumed to mix without change. Be able to cite evidence of a chemical change for every equation written.

The first time a new substance is encountered its name should be given and its properties described. Thereafter, merely indicate whether it is a gas, solution, or precipitate by the convention described above.

Record of Unknowns.—Many forms have been devised for recording the results of the analyses on unknown substances. The following is recommended as not only convenient but as providing a systematic arrangement of results and requiring only a small amount of time of the student:

SPECIMEN NOTES ON THE ANALYSIS OF AN UNKNOWN

Unknown No. 9.	Analysis begun: Oct. 1.
Serial Number: 641.	Analysis completed: Oct. 3.
Nature of unknown: Yellow alloy.	Date due: Oct. 5.

Solvent: Warm dilute HNO_3, giving a green solution.

No.	Substance	Treatment	Result	Inference
1	Alloy	Dilute HNO_3	Green solution	Cu (?)
2	Solution #1	Evaporation	Green residue	
3	Residue #2	HCl, H_2O	Solution	No Ag
4	Solution #3	H_2S	Dark precipitate	Cu subgroup
5	Precipitate #4	NH_4OH, H_2O_2, H_2S	Dark residue	Cu subgroup
6	Residue #5	Dilute HNO_3	Solution, S residue	No Hg
7	Solution #6	H_2SO_4, evaporate, dilute	Slight white precipitate	Pb (?)
8	Precipitate #7	NaOH	Solution	
9	Solution #8	$K_2Cr_2O_7$, $HC_2H_3O_2$	Slight yellow precipitate	Pb (trace)?
10	Filtrate #7	NH_4OH	Deep blue solution	Cu
11	Solution #10	NaCN, H_2S	No effect	No Cd
12	Filtrate #5	Dilute HCl	White precipitate	S (?)
13	Precipitate #10	HCl, alcohol	White residue	
14	Residue #13	HNO_3, $AgNO_3$, $NH_4C_2H_3O_2$	No effect	No As
15	Filtrate #13	Al wire	No effect	No Sb
16	Solution #15	$HgCl_2$	No effect	No Sn
17	Filtrate #4	NH_4OH, H_2S	White precipitate	Al or Zn
18	Precipitate #17	Dilute HCl	Colorless solution	No Co or Ni
19	Solution #18	NaOH, Na_2O_2	Colorless solution	No Fe subgr.
20	Solution #19	HNO_3, NH_4OH	No effect	No Al
21	Solution #20	Divide		
22	Solution #21	HNO_3, H_2O_2, ether	No effect	No Cr
23	Solution #21	H_2S	White precipitate	Zn
24	Solution #17	$(NH_4)_2CO_3$	No effect	No Gr. IV
25	Solution #24	Na_2HPO_4	No effect	No Mg

Reported: Cu, Zn. Omitted: Pb. Material: Brass (with lead).

Remarks: Pb was not reported because the precipitates in reactions 7 and 9 looked too small to be considered dependable tests.

Grade............ Instructor's signature:....................

Note.—The number in the second column of the table refers to the line in which the substance was formed; *e.g.*, filtrate #4 in line 17 means the filtrate from the precipitation by H_2S, as mentioned in line 4; it does not mean the fourth filtrate in the analysis.

After an analysis has been reported, the student should discuss with his instructor any mistakes and enter under the heading "Remarks" explanations of the errors in the procedure that caused erroneous inferences. These reports must be graded or viséed by the instructor before other unknowns will be issued to the student.

UNKNOWNS

Issuing Unknowns.—Substances for analysis are obtained at the storeroom on cards furnished by the instructor. The following is suggested as a very convenient form of card for the purpose:

QUALITATIVE ANALYSIS REPORT CARD

Name.......................... Unknown No..............
Desk.......................... Serial No................
Date Issued.................... Grade...................
Date Reported..................

	Group I	Group II	Group III	Group IV	Group V	
Cations						
Anions						Group VI

Instructor's Signature..........................

It is suggested that, before issuing the card for the unknown, the instructor give the student a brief oral quiz, so as to be sure that the latter is ready to begin the analysis, and that he has an adequate understanding of how to proceed. The lists of exercises at the ends of the blocks of preliminary experiments contain questions suitable for these quizzes.

In issuing the card, the instructor should fill in the date and the series or group of unknowns and should sign his name (or initials). The storekeeper will enter the serial number of the unknown issued and on his own record both the serial number and the corresponding code number. A very satisfactory code for unknowns consists of a number or a letter to indicate the series or group of unknowns (corresponding to "Unknown No......." on the card) and a second number showing the number of the unknown in that series; for example, I-6 or D-14. The entries in the storekeeper's record will then be of the following type:

643—I-6
644—III-2
645—V-14, etc.

The code numbers for unknowns must never be told to students, and the storekeeper's records should be carefully protected from spying.

When the student has finished his analysis he will enter in the proper squares the ions found and turn the card in at the storeroom. The instructor will later grade the analysis, and the card will be filed as a permanent record in the storeroom.

THE ELECTROMOTIVE SERIES

In the following list the metals are arranged in the order of their decreasing "electrolytic solution tension," *i.e.*, in the order of their decreasing tendency to pass from the metallic into the ionic condition. Potassium, with the greatest tension, is at the top of the list, and gold, with the smallest, is at the bottom. This order corresponds, in a rough way, to the reactivity of the metals. The less common metals are omitted.

Potassium
Sodium
Magnesium
Aluminum
Manganese
Zinc
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Copper
Arsenic
Bismuth
Antimony
Mercury
Silver
Platinum
Gold

This list has certain valuable applications in qualitative analysis:

1. Any metal will displace from solution (*i.e.*, from its ionic form) any metal coming below it in the list; *e.g.*, Fe will displace Cu, but not Cd.

2. Metals occurring above hydrogen will dissolve in non-oxidizing acids like HCl or dilute H_2SO_4; metals occurring below hydrogen will require oxidizing solvents like HNO_3, concentrated H_2SO_4, or aqua regia.

The student is referred to textbooks on general and physical chemistry for the electrochemical applications of this series.

REAGENTS

The following is a list of the reagents required for this course. In the case of solutions, the composition and mode of preparation are indicated.

DESK REAGENTS

Acetic Acid, 6M.—Dilute 350 ml. of glacial acetic acid with 650 ml. of water.

Ammonium Carbonate, 2M.—Dissolve 250 grams of solid $(NH_4)_2CO_3$ in 1 liter of $6M$ NH_4OH.

Ammonium Chloride, 2M.—Dissolve 107 grams of c.p. NH_4Cl in 1 liter of water.

Ammonium Hydroxide, 6M.—Dilute 400 ml. of the concentrated ammonia water of commerce (28 per cent NH_3; sp. gr. = 0.90) with 600 ml. of water.

Ammonium Oxalate, 0.3M.—Dissolve 40 grams of $(NH_4)_2C_2O_4.H_2O$ in 1 liter of warm water.

Ammonium Polysulfide, 3M.—Place 200 ml. of concentrated NH_4OH and 25 grams of sulfur (flowers) in a large bottle, saturate the mixture with H_2S, add 200 ml. of concentrated NH_4OH, and dilute to 1 liter. Shake well and filter or decant.

Barium Chloride, 0.5M.—Dissolve 120 grams of $BaCl_2.2H_2O$ in 1 liter of warm water.

Concentrated Hydrochloric Acid, 12M.—Use the concentrated c.p. acid of commerce (37 per cent HCl; sp. gr. = 1.19).

Dilute Hydrochloric Acid, 6M.—Dilute 500 ml. of concentrated HCl with 500 ml. of water; sp. gr. = 1.12.

Concentrated Nitric Acid, 16M.—Use the concentrated c.p. HNO_3 of commerce (69 per cent HNO_3; sp. gr. = 1.42).

Dilute Nitric Acid, 6M.—Dilute 380 ml. of concentrated HNO_3 with 620 ml. of water; sp. gr. = 1.20.

Concentrated Sulfuric Acid, 18M.—Use the concentrated c.p. acid of commerce (95 per cent H_2SO_4; sp. gr. = 1.84).

Dilute Sulfuric Acid, 3M.—Pour 200 ml. of concentrated H_2SO_4 slowly into 1,000 ml. of water, stirring constantly; sp. gr. = 1.19.

Lead Acetate, 0.3M.—Dissolve 114 grams of $Pb(C_2H_3O_2)_2.3H_2O$ in 1 liter of water. Filter if necessary.

Potassium Dichromate, 0.3M.—Dissolve 90 grams of $K_2Cr_2O_7$ in 1 liter of hot water.

Potassium Ferrocyanide, 0.5M.—Dissolve 105 grams of $K_4Fe(CN)_6.3H_2O$ in 1 liter of water.

Silver Nitrate, 0.3M.—Dissolve 51 grams of $AgNO_3$ in 1 liter of water.

Sodium Phosphate, 0.25M.—Dissolve 90 grams of $Na_2HPO_4.12H_2O$ in 1 liter of hot water.

SIDE SHELF

Liquids

Alcohol.—Ethyl, methyl, or denatured may be used.

Aluminon (0.1 per cent).—Dissolve 1 gram of aurin tricarboxyllic acid in a small amount of dilute NH_4OH and dilute to 1 liter.

Aluminum Sulfate, 0.3M.—Dissolve 200 grams of $Al_2(SO_4)_3.18H_2O$ in 1 liter of warm water.

Ammonium Acetate (10 per cent).—Dissolve 100 grams of $NH_4C_2H_3O_2$ in 900 ml. of water.

Ammonium Acetate (50 per cent).—Dissolve 500 grams of $NH_4C_2H_3O_2$ in 500 ml. of water. Mark bottle, "For use in (**65**) only."

Ammonium Iodide, M.—Dissolve 145 grams of NH_4I in 1 liter of water. The solution will turn brown, owing to oxidation by air, but that does not matter.

Ammonium Molybdate.—Dissolve 50 grams of molybdic anhydride, MoO_3, in a mixture of 125 ml. of water and 75 ml. of concentrated NH_4OH (sp. gr. = 0.90). Slowly add this mixture with constant stirring to a mixture of 250 ml. of concentrated HNO_3 and 550 ml. of water. Allow to stand in a warm place for several days and then decant the clear solution. This solution is $0.35M$ in H_2MoO_4, M in NH_4NO_3, and $3M$ in HNO_3.

Ammonium Nitrate, M.—Dissolve 80 grams of NH_4NO_3 in 1 liter of water.

Ammonium Sulfate, M.—Dissolve 130 grams of $(NH_4)_2SO_4$ in 1 liter of water.

Ammonium Thiocyanate, M.—Dissolve 75 grams of NH_4SCN in 1 liter of water.

Amyl Alcohol-Ether Mixture.—Add 350 ml. of amyl alcohol to 650 ml. of ethyl ether. Keep in glass-stoppered bottle. Mark, "For use in Co^{++} test only."

Antimony Trichloride, 0.4M.—Dissolve 56.5 grams of $SbCl_3$ in 70 ml. of concentrated HCl and dilute to 1 liter. Add a little HCl to dissolve any turbidity.

Arsenic Acid, M.—Dissolve 150 grams of H_3AsO_4 in 1 liter of hot water.

Arsenic Trichloride, 0.2M.—Dissolve 20 grams of As_2O_3 in 120 ml. of hot concentrated HCl and dilute to 1 liter.

Barium Acetate, 0.5M.—Dissolve 137 grams of $Ba(C_2H_3O_2)_2.H_2O$ in 1 liter of water.

Barium Chloride, M.—Dissolve 208 grams of $BaCl_2$ in 1 liter of water.

Barium Nitrate, 0.4M.—Dissolve 95 grams of $Ba(NO_3)_2$ in 1 liter of warm water.

Barium Nitrate–Calcium Nitrate Mixture.—Dissolve 5 grams of $Ba(NO_3)_2$ and 25 grams of $Ca(NO_3)_2$ in 1 liter of warm water.

Bismuth Nitrate, 0.1M.—Dissolve 48 grams of $Bi(NO_3)_3$ in 50 ml. of concentrated HNO_3 and dilute to 1 liter. If a turbidity appears, add more HNO_3.

Bromine Solution (**saturated**).—Add bromine to water, with shaking, until a small excess remains undissolved.

Cadmium Nitrate, 0.5M.—Dissolve 154 grams of $Cd(NO_3)_2.4H_2O$ in 1 liter of water.

Calcium Hydroxide (**saturated solution**).—Slake 3 or 4 grams of high-grade quicklime with an excess of warm water. Add 1 liter of water, shake thoroughly, and filter.

Calcium Nitrate, M.—Dissolve 236 grams of $Ca(NO_3)_2.4H_2O$ in 1 liter of water.

Calcium Sulfate (**saturated**).—To 1 liter of water add 6 ml. of dilute H_2SO_4 and 2 grams of precipitated $CaCO_3$. Shake thoroughly and allow to stand until solution is neutral to methyl orange. Add more $CaCO_3$ if necessary.

Carbon Tetrachloride.—Keep in glass-stoppered bottle.

Chlorine Solution (**saturated**).—Bubble a slow current of chlorine through 1 liter of water until the latter is saturated. (Hood.) The gas is most conveniently obtained from a cylinder of compressed chlorine. If this is not available, the gas may be prepared by placing some solid $KMnO_4$ in a small generator fitted with a dropping funnel and a delivery tube and allowing concentrated HCl from the funnel to drip slowly upon the $KMnO_4$. Keep the solution in a brown glass-stoppered bottle.

Chromium Chloride, 0.2M.—Dissolve 53 grams of $CrCl_3.6H_2O$ in 20 ml. of concentrated HCl and 980 ml. of water.

Cobalt Nitrate, 0.2M.—Dissolve 58 grams of $Co(NO_3)_2.6H_2O$ in 1 liter of water.

Cobalt Nitrate, 4M (**saturated**).—Dissolve a kilogram of $Co(NO_3)_2.6H_2O$ in 1 liter of water. Mark, "For use in (**124**) only."

Copper Nitrate, 0.2M.—Dissolve 59 grams of $Cu(NO_3)_2.6H_2O$ in 1 liter of water.

Copper Sulfate, M.—Dissolve 250 grams of $CuSO_4.5H_2O$ in 1 liter of water.

Dimethylglyoxime, 0.1M.—Dissolve 12 grams of the solid in 1 liter of 95 per cent alcohol.

Ether.—Use ethyl ("sulfuric") ether. Keep in a glass-stoppered bottle.

Ferric Chloride, 0.4M.—Dissolve 108 grams of $FeCl_3.6H_2O$ in 10 ml. of concentrated HCl and 990 ml. of water.

Ferric Sulfate, 0.2M.—Dissolve 112 grams of $Fe_2(SO_4)_3.9H_2O$ in 20 ml. of dilute H_2SO_4 and 980 ml. of water.

Ferrous Sulfate, M.—Dissolve 392 grams of $FeSO_4.(NH_4)_2SO_4.6H_2O$ in 500 ml. of dilute H_2SO_4 and 500 ml. of water.

Hydrochloric Acid, M.—Dilute 85 ml. of concentrated HCl to 1 liter.

Hydrogen Peroxide.—Use ordinary commercial solution (3 per cent). Keep in glass-stoppered bottle.

Iodine–Potassium Iodide Solution.—Dissolve 25 grams of KI and 12.7 grams of I_2 in 50 ml. of water and dilute to 1 liter.

Lanthanum Nitrate (5 per cent).—Dissolve 50 grams of $La(NO_3)_3.6H_2O$ in 1 liter of water.

Lead Chloride (saturated).—Dissolve 11 grams of $PbCl_2$ in 1 liter of hot water. Cool and decant from any precipitate.

Lead Nitrate, 0.5M.—Dissolve 165 grams of $Pb(NO_3)_2$ in 1 liter of water.

Magnesium Nitrate, 0.5M.—Dissolve 130 grams of $Mg(NO_3)_2.6H_2O$ in 1 liter of water.

Manganous Chloride-Hydrochloric Acid Mixture.—A saturated solution of $MnCl_2.4H_2O$ in concentrated HCl.

Manganous Nitrate, 0.5M.—Dissolve 144 grams of $Mn(NO_3)_2.4H_2O$ in 1 liter of water.

Manganous Nitrate (50 per cent).—Use the commercial $Mn(NO_3)_2$, undiluted. Mark, "For use in (**111**) and (**154**) only."

Mercuric Chloride, 0.2M.—Dissolve 54 grams of $HgCl_2$ in 1 liter of water.

Mercuric Nitrate, 0.2M.—Dissolve 68 grams of $Hg(NO_3)_2.H_2O$ in 1 liter of water. If the mixture is turbid, add a little concentrated HNO_3.

Mercurous Nitrate, 0.5M.—Dissolve 280 grams of $Hg_2(NO_3)_2.2H_2O$ in 300 cc. of concentrated HNO_3 and 700 ml. of water.

Methyl Orange Solution.—Dissolve 0.2 gram of the solid in 1 liter of warm water. Decant from any residue.

Nickel Nitrate, 0.3M.—Dissolve 83 grams of $Ni(NO_3)_2.6H_2O$ in 1 liter of water.

p-**Nitrobenzeneazoresorcinol (0.1 per cent).**—Dissolve 1 gram of the dye in 10 ml. of 6*M* NaOH and dilute to 1 liter.

Perchloric Acid, 11M.—Use the 70 to 72 per cent solution.

Phenolphthalein (0.1 per cent).—Dissolve 1 gram of the solid in 1 liter of 95 per cent C_2H_5OH.

Potassium Arsenate, 0.2M.—Dissolve 51 grams of K_3AsO_4 in 1 liter of water.

Potassium Bromide, M.—Dissolve 120 grams of KBr in 1 liter of water.

Potassium Chloride, M.—Dissolve 75 grams of KCl in 1 liter of water.

Potassium Chromate, 0.5M.—Dissolve 97 grams of K_2CrO_4 in 1 liter of water.

Potassium Ferricyanide, 0.3M.—Dissolve 100 grams of $K_3Fe(CN)_6$ in 1 liter of water.

Potassium Iodide, M.—Dissolve 166 grams of KI in 1 liter of water.

Potassium Permanganate, 0.1M.—Dissolve 16 grams of $KMnO_4$ in 1 liter of water.

Potassium Sodium Tartrate, 0.25M.—Dissolve 70 grams of $KNaC_4H_4O_6.4H_2O$ in 1 liter of water.

Sodium Acetate, 3M.—Dissolve 408 grams of $NaC_2H_3O_2$ in 1 liter of hot water.

Sodium Arsenite, M.—Add 100 grams of As_2O_3 to 500 ml. of 6*M* NaOH, boil gently for 10 or 15 min., and dilute to 1 liter. After standing, decant the clear solution from any residue.

Sodium Carbonate, M.—Dissolve 106 grams of anhydrous Na_2CO_3 in 1 liter of water.

Sodium Chloride, M.—Dissolve 58.5 grams of NaCl in 1 liter of water.

Sodium Cyanide, M.—Dissolve 50 grams of NaCN in 1 liter of water.

Sodium Fluoride.—Dissolve 42 grams of NaF in 1 liter of warm water.

Sodium Hydroxide (0.1 per cent).—Dissolve 1 gram of the best grade of NaOH (chloride-free) in 1 liter of water.

Sodium Hydroxide, 6M.—Dissolve 250 grams of NaOH "purified by alcohol" in 1 liter of water.

Sodium Nitrate, M.—Dissolve 85 grams of $NaNO_3$ in 1 liter of water.

Sodium Nitrite, M.—Dissolve 69 grams of $NaNO_2$ in 1 liter of water.

Sodium Silicate.—Dilute 50 ml. of water glass to 1 liter. If a sediment forms on standing, decant the clear liquid.

Sodium Sulfate, M.—Dissolve 322 grams of $Na_2SO_4.10H_2O$ (Glauber's salt) in 1 liter of water.

Sodium Sulfide, M.—Dissolve 240 grams of $Na_2S.9H_2O$ in 1 liter of water.

Sodium Sulfite, M.—Dissolve 126 grams of Na_2SO_3 in 1 liter of water.

Sodium Tetraborate (Borax), 0.1M.—Dissolve 40 grams of $Na_2B_4O_7.10H_2O$ in 1 liter of water.

Sodium Thiosulfate, 0.5M.—Dissolve 125 grams of $Na_2S_2O_3.5H_2O$ in 1 liter of water.

Stannic Chloride, 0.2M.—Dissolve 52 grams of $SnCl_4$ in 100 ml. of concentrated HCl and dilute to 1 liter.

Stannous Chloride, 0.5M.—Dissolve 115 grams of $SnCl_2.2H_2O$ in 170 ml. of concentrated HCl and dilute to 1 liter. A little granulated tin kept in the bottle will prevent oxidation to $SnCl_4$.

Strontium Nitrate, 0.5M.—Dissolve 142 grams of $Sr(NO_3)_6.4H_2O$ in 1 liter of water.

Strontium Sulfate (saturated solution).—To 1 liter of water add 6 ml. of dilute H_2SO_4 and 2 grams of precipitated $SrCO_3$. Let stand several days with occasional shaking. If there is no undissolved residue, or if the solution is still acid to litmus, add more $SrCO_3$ and repeat the procedure. Decant or filter.

Tartaric Acid, M.—Dissolve 168 grams of $H_2C_4H_4O_6.H_2O$ in 1 liter of water.

Zinc Nitrate, 0.3M.—Dissolve 89 grams of $Zn(NO_3)_2.6H_2O$ in 1 liter of water.

Zinc Perchlorate, M.—Dissolve 372 grams of $Zn(ClO_4)_2.6H_2O$ in 1 liter of water. If this salt is not available, dilute 66 ml. of 70 per cent $HClO_4$ to about 400 ml. and add about 80 grams of metallic zinc and a few milliliters of $Cu(ClO_4)_2$ solution (prepared by dissolving metallic copper in $HClO_4$).

Let the mixture stand in a warm place until the solution is neutral. If still acid, add a little $ZnCO_3$ (free from Na_2CO_3).

Zinc Uranyl Acetate.—Mix 100 grams of $UO_2(C_2H_3O_2)_2.2H_2O$ with 60 ml. of $HC_2H_3O_2$ and make up to 500 ml. Mix 300 grams of $Zn(C_2H_3O_2)_2.2H_2O$ with 60 ml. of $HC_2H_3O_2$ and make up to 500 ml. Combine the mixtures and let stand in a warm place, shaking occasionally, for several days before decanting or filtering.

Solids

Aluminum (wire cut into pieces weighing approximately 0.05 gram).
Ammonium chloride.
Borax.
Calcium carbonate (powdered).
Calcium fluoride (powdered).
Calcium oxalate.
Calcium phosphate (powdered).
Charcoal.
Iron (brads).
Iron pyrites (powdered).
Lead (sheet, pieces).
Manganese dioxide, c.p.
Microcosmic salt, $NaNH_4HPO_4$.
Potassium bromide.
Potassium chlorate, c.p.
Potassium dichromate.
Potassium hydrogen sulfate.
Potassium iodide.
Silica (powdered).
Sodium acetate.
Sodium bismuthate.
Sodium carbonate (anhydrous, c.p.).
Sodium chloride.
Sodium fluoride.
Sodium nitrate (crystals).
Sodium nitrite.
Sodium oxalate.
Sodium peroxide.
Sodium sulfide (keep in rubber-stoppered bottle).
Sodium sulfite.
Sodium thiosulfate.
Starch iodide paper.
Tartaric acid.
Tin (granulated).
Turmeric paper.
Zinc (dust).
Zinc (mossy).

LABORATORY EQUIPMENT

Reagent Bottles.—The most satisfactory device for delivering small amounts of solution is a pipette fitted with a rubber bulb. Bottles fitted with these pipettes (Fig. 16) may be bought from dealers in chemical supplies; or ordinary bottles may be equipped with homemade pipettes and rubber bulbs. Some teachers like to convert the reagent bottles used in general chemistry into dropping bottles by storing the glass stoppers and using pipettes during the time in which semimicro analysis is given. The rubber bulbs have short lives and must be replaced from time to time.

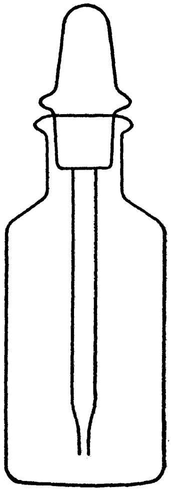
FIG. 16.

The size of the bottle is determined by the size of the class and by whether or not each student is to be furnished with an individual set of reagents. For classes of 50 to 100 students, a convenient size for side-shelf reagents is 250 ml.; for desk reagents, 125 ml.; and for individual reagents, 60 ml.

Centrifuges.—Several small centrifuges for 10-ml. test tubes should be provided, at least one for every six students. It is also desirable to have a larger instrument that can be used for volumes of about 50 ml.

Individual Apparatus.—The apparatus for the student lockers may vary within wide limits, according to the organization of the laboratory. The following lists are merely suggestive. In case the desks are already equipped with outfits for general chemistry, it will be necessary to add only the apparatus listed as micro equipment, and some extra glass tubing for making pipettes and extra glass rods for making stirring rods.

Macro Apparatus

1 beaker, Griffin, 400 ml.
4 beakers, Griffin, 150 ml.
2 beakers, Griffin, 100 ml.
2 burners, Bunsen
1 casserole, 210 ml.
1 clamp, Bunsen
1 clamp holder
1 crucible, No. 0
1 dish, porcelain, 80 ml.
1 filter stand
1 flask, Florence, 500 ml.
2 flasks, Erlenmeyer, 300 ml.
2 flasks, Erlenmeyer, 125 ml.
1 flask, Erlenmeyer, 50 ml.
1 flask, filter, 250 ml.
1 forceps, iron
2 funnels, glass, 70 mm.
1 funnel, Büchner, 50 mm.
2 glasses, cobalt
1 mortar and pestle, 110 mm.
1 spatula, nickel or monel
1 stand, iron, with 2 rings
12 test tubes, pyrex, 15 by 150 mm.
1 test-tube brush
1 test-tube holder
1 test-tube rack
1 thistle tube
1 triangle, nichrome
2 watch glasses, 75 mm.
2 watch glasses, 100 mm.
1 wing top for burner

Micro Equipment

1 burner, micro
1 casserole, 30 ml.
12 test tubes, 10 by 75 mm.
1 test-tube brush, micro
1 test-tube rack, micro
1 watch glass, 60 mm.

Non-returnable Apparatus

1 box matches
1 file, triangular
5 ft. glass tubing, 5 mm.
5 ft. glass tubing, 7 mm.
5 ft. glass rod, 3 mm.
1 platinum wire in glass holder
1 ft. rubber tubing, black gum, 6 mm.
5 ft. rubber tubing, 9 mm., for gas connections
1 towel
1 vial litmus paper, blue
1 vial litmus paper, red
1 wire gauze

TABLE OF SOLUBILITIES

	Acetate	Arsenate	Arsenite	Borate	Bromide	Carbonate	Chlorate	Chloride
Aluminium.	Water	Acids	(3)	Acids	Water	. . . . .	Water	Water
Ammonium.	Water	Water	Water	Water	Water	Water	Water	Water
Antimony.	. . . . .	. . . . .	. . . . .	. . . . .	HBr	. . . . .	. . . . .	HCl
Arsenic.	. . . . .	. . . . .	. . . . .	. . . . .	HBr	. . . . .	. . . . .	HCl
Barium.	Water	Acids	Acids	Acids (2)	Water	Acids	Water	Water
Bismuth.	Water	Acids	. . . . .	Acids	HBr	Acids	Water	HCl
Cadmium.	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Calcium.	Water	Acids	Acids	(1)	Water	Acids	Water	Water
Chromium (ic).	Water	Acids	(3)	Acids	Water	. . . . .	Water	Water or Insol.
Cobalt.	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Copper (cupric).	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Ferric.	Cold Water	Acids	Acids	Acids	Water	. . . . .	Water	Water
Ferrous.	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Lead.	Water	HNO_3	HNO_3	HNO_3	(1)	HNO_3	Water	Hot water
Magnesium.	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Manganese.	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Mercuric.	Water	Acids	Acids	. . . . .	Water	Acids	Water	Water
Mercurous.	(1)	Acids	Acids	. . . . .	HNO_3 Br_2	HNO_3	Water	HNO_3 Cl_2
Nickel.	Water	Acids	Acids	Acids	Water	Acids	Water	Water
Potassium.	Water	Water	Water	Water	Water	Water	Water	Water
Silver.	(1)	HNO_3	HNO_3	HNO_3	KCN	HNO_3	Water	NH_4OH KCN
Sodium.	Water	Water	Water	Water	Water	Water	Water	Water
Stannic.	Water	Acids	. . . . .	. . . . .	Water	. . . . .	. . . . .	Water
Stannous.	Water	Acids	Acids	Acids	Water	. . . . .	. . . . .	Water
Strontium.	Water	Acids	Acids	(1)	Water	Acids	Water	Water
Zinc.	Water	Acids	Acids	Acids	Water	Acids	Water	Water

Key to Abbreviations and References.—"Alks." = NaOH, KOH; "Insol." = insoluble in acids; (1) = slightly soluble in water; (2) = soluble in solutions of ammonium salts; (3) = hydrolyzed by water; (4) = soluble in ammonium acetate solution; (5) = acid of anion decomposed with precipitate formation.

(6) Many insoluble cyanides, oxalates, tartrates, and thiosulfates are soluble in solutions of salts containing the anion involved. (7) Native silicates are generally insoluble in acids; decomposition by acids is limited almost wholly to precipitated silicates.

TABLE OF SOLUBILITIES (*Continued*)

	Chromate	Cyanide (6)	Ferricyanide	Ferrocyanide	Fluoride	Fluosilicate	Hydroxide
Aluminium	Acids	(3)	.....	Acids	Water	Water	Acids Alks.
Ammonium	Water	Water	Water	Water	Water	Water (3)	Water
Antimony	.....	.....	.....	.....	(1)	.....	Acids Alks.
Arsenic	.....	.....	.....	.....	.....	.....	Acids Alks.
Barium	Acids	(1)	Water	Water	HNO_3	Acids	(1)
Bismuth	Acids	(3)	.....	Acids	Acids	Water	Acids
Cadmium	Acids	(1)	.....	.....	(1)	Water	Acids NH_4OH
Calcium	Water	Water	Water	(1)	Insol.	(1)	(1)
Chromium (ic)	Acids	.....	.....	.....	Water	Water	Acids
Cobalt	Acids	Acids	Insol.	Insol.	(1)	Water	Acids NH_4OH
Copper (cupric)	Water	.....	Insol.	Insol.	(1)	Water	Acids NH_4OH
Ferric	Water	.....	Water	Insol.	(1)	Water	Acids
Ferrous	.....	.....	Insol.	Insol.	(1)	Water	Acids
Lead	HNO_3	(1)	(1)	Insol.	(1)	Water	HNO_3 Alks.
Magnesium	Water	Water	Water	Water	Acids	Water	Acids (2)
Manganese	Acids	.....	Insol.	Acids	Acids	Water	Acids
Mercuric	Acids	Water	.....	Acids	Water	Water	
Mercurous	Acids	.....	Acids	.....	Water	(1)	
Nickel	Acids	Hot acids	Insol.	Insol.	(1)	Water	Acids NH_4OH
Potassium	Water	Water	Water	Water	Water	(1)	Water
Silver	HNO_3	Conc. HNO_3	Insol.	Insol.	Water	Water	
Sodium	Water	Water	Water	Water	Water	(1)	Water
Stannic	Acid	.....	.....	Insol.	.....	Water	Acids Alks.
Stannous	.....	.....	.....	Insol.	.....	Water	Acids Alks.
Strontium	(1)	Water	Water	Water	Acids	Water	(1)
Zinc	Acids	Acids	Acids	Insol.	Acids	Water	Acids Alks. NH_4OH

Key to Abbreviations and References.—"Alks." = NaOH, KOH; "Insol." = insoluble in acids; (1) = slightly soluble in water; (2) = soluble in solutions of ammonium salts; (3) = hydrolyzed by water; (4) = soluble in ammonium acetate solution; (5) = acid of anion decomposed with precipitate formation.

(6) Many insoluble cyanides, oxalates, tartrates, and thiosulfates are soluble in solutions of salts containing the anion involved. (7) Native silicates are generally insoluble in acids; decomposition by acids is limited almost wholly to precipitated silicates.

TABLE OF SOLUBILITIES (*Continued*)

	Iodide	Nitrate	Nitrite	Oxalate (6)	Oxide	Perchlorate	Permanganate	Phosphate
Aluminium	Water	Water	(3)	Acids	Acids or Insol.	Water	Water	Acids
Ammonium	Water	Water	Water	Water	.....	Water	Water	Water
Antimony	(3)	.....	(3)	.....	Acids Alks.			
Arsenic	Water	.....	.....	.....	Acids Alks.			
Barium	Water	Water	Water	Acids	(1)	Water	Water	Acids
Bismuth	Acids	HNO_3	(3)	Acids	Acids	.....	.....	Acids
Cadmium	Water	Water	Water	Acids	Acids	Water	Water	Acids
Calcium	Water	Water	Water	Strong acids	(1)	Water	Water	Acids
Chromium (ic)	Water	Water	(3)	(1)	Acids or Insol.	Water	Water	Acids
Cobalt	Water	Water	Water	Acids	Acids	Water	Water	Acids
Copper (cupric)	.....	Water	Water	Acids	Acids	Water	Water	Acids
Ferric	Water	.....	Water	Acids	Acids	Water	Water	Acids
Ferrous	Water	Water	Water	Acids	Acids	.....	.....	Acids
Lead	(1)	Water	Water	HNO_3	Acids	Water	Water	HNO_3
Magnesium	Water	Water	Water	Water	Acids	Water	Water	Acids
Manganese	Water	Water	Water	Acids	Acids	Water	Water	Acids
Mercuric	Acids	Water	Water	Acids	Acids	Water	Water	Acids
Mercurous	HNO_3	HNO_3	(3)	HNO_3	HNO_3	Water	.....	HNO_3
Nickel	Water	Water	Water	Acids	Acids	Water	Water	Acids
Potassium	Water	Water	Water	Water	.....	(1)	Water	Water
Silver	KCN	Water	(1)	HNO_3	HNO_3	Water	Water	HNO_3
Sodium	Water	Water	Water	Water	.....	Water	Water	Water
Stannic	(3)	.....	(3)	Water	Acids Alks. Insol.	Water	Water	Acids
Stannous	Water	.....	.....	Acids	Acids Alks.	Water	.....	Acids
Strontium	Water	Water	Water	Acids	(1)	Water	Water	Acids
Zinc	Water	Water	Water	Acids	Acids	Water	Water	Acids

Key to Abbreviations and References.—"Alks." = NaOH, KOH; "Insol." = insoluble in acids; (1) = slightly soluble in water; (2) = soluble in solutions of ammonium salts; (3) = hydrolyzed by water; (4) = soluble in ammonium acetate solution; (5) = acid of anion decomposed with precipitate formation.

(6) Many insoluble cyanides, oxalates, tartrates, and thiosulfates are soluble in solutions of salts containing the anion involved; (7) Native silicates are generally insoluble in acids; decomposition by acids is limited almost wholly to precipitated silicates.

TABLE OF SOLUBILITIES (*Continued*)

	Silicate (7)	Sulfate	Sulfide	Sulfite	Tartrate (6)	Thiocyanate	Thiosulphate (6)
Aluminium	Acids (5)	Water	(3)	Acids	Water	Water	**Water**
Ammonium	(3)	Water	Water	Water	Water	Water	**Water**
Antimony	.....	.....	Conc. acids	.....	Acids		
Arsenic	.....	.....	HNO_3 or Aqua Regia				
Barium	Acids (5)	Insol.	(3) (2)	Acids	Acids	Water	**(1)** *
Bismuth	Acids (5)	H_2SO_4	HNO_3	.....	Acids		
Cadmium	Acids (5)	Water	Acids	Acids	(1)	(1)	**Water**
Calcium	Acids (5)	(1)	(3)	Acids	Acids	Water	**Water**
Chromium (ic)	Acids (5)	Water	(3)	.....	Water	Water	
Cobalt	Acids (5)	Water	HNO_3	Acids	Water	Water	**Water**
Copper (cupric)	Acids (5)	Water	HNO_3	Acids	Water		
Ferric	Acids (5)	Water	Acids	.....	Water	Water	
Ferrous	Acids (5)	Water	Acids	Acids	(1)	Water	**Water**
Lead	HNO_3 (5)	(4)	HNO_3	HNO_3	HNO_3	(1)	**HNO_3 (5)**
Magnesium	Acids (5)	Water	(3) (2)	Water	Water	Water	**Water**
Manganese	Acids (5)	Water	Acids	Acids	(1)	Water	**Water**
Mercuric	.....	H_2SO_4	Aqua Regia	Acids	Acids	(1)	
Mercurous	.....	(1)	Aqua Regia	.....	(1)	Acids	
Nickel	Acids (5)	Water	HNO_3	Acids	Acids	Water	**Water**
Potassium	Water	Water	Water	Water	Water	Water	**Water**
Silver	HNO_3 (5)	Water	Conc. HNO_3	HNO_3	HNO_3	HNO_3 (5)	**HNO_3 (5)**
Sodium	Water	Water	Water	Water	Water	Water	**Water**
Stannic	.....	H_2SO_4	Acids	.....	Water	Water	**Water**
Stannous	.....	H_2SO_4	Acids	Acids	Acids	Water	**Water**
Strontium	Acids (5)	Insol.	(3) (2)	Acids	Acids	Water	**Water**
Zinc	Acids (5)	Water	Acids	Acids	Acids	Water	**Water**

Key to Abbreviations and References.—"Alks." = NaOH, KOH; "Insol." = insoluble in acids; (1) = slightly soluble in water; (2) = soluble in solutions of ammonium salts; (3) = hydrolyzed by water; (4) = soluble in ammonium acetate solution; (5) = acid of anion decomposed with precipitate formation.

(6) Many insoluble cyanides, oxalates, tartrates, and thiosulfates are soluble in solutions of salts containing the anion involved. (7) Native silicates are generally insoluble in acids; decomposition by acids is limited almost wholly to precipitated silicates.

PERIODIC SYSTEM

		Group 0	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
	Type Compound		E_2O	EO	E_2O_3	EH_4, EO_2	EH_3, E_2O_5	EH_2, EO_3	EH, E_2O_7	EO_4
	Valence	0	+1	+2	+3	−4, +4	−3, +5	−2, +6	−1, +7	+8
PERIODS	1	He, 4	Li, 7	Be, 9	B, 11	C, 12	N, 14	O, 16	F, 19	
	2	Ne, 20.2	Na, 23	Mg, 24.3	Al, 27	Si, 28.1	P, 31.0	S, 32.1	Cl, 35.5	
	3	A, 39.9	K, 39.1	Ca, 40.1	Sc, 45.1	Ti, 48.1	V, 51.0	Cr, 52.0	Mn, 54.9	Fe, 55.8; Co, 59; Ni, 58.7
	4		Cu, 63.6	Zn, 65.4	Ga, 69.7	Ge, 72.6	As, 75	Se, 79.2	Br, 79.9	
	5	Kr, 82.9	Rb, 85.5	Sr, 87.6	Y, 89	Zr, 91.2	Cb, 93.5	Mo, 96.0	Ma	Ru, 101.7; Rh, 102.9; Pd, 106.7
	6		Ag, 107.9	Cd, 112.4	In, 114.8	Sn, 118.7	Sb, 121.8	Te, 127.5	I, 126.9	
	7	X, 130.2	Cs, 132.8	Ba, 137.4	La, 138.9	Ce, 140.2	Nd, 144.3	....	....	
	8	....	....	....	Rare earths not placed	....	....	....	....	
	9	....	....	....	Yb, 173.5	....	Ta, 181.5	W, 184	Re	Os, 190.9; Ir, 193.1; Pt, 195.2
	10		Au, 197.2	Hg, 200.6	Tl, 204.0	Pb, 207.2	Bi, 209	RaA	....	
	11	Rn, 222.0	....	Ra, 226.0	Ac	Th, 232.1	Ux	U, 238.2	....	

INDEX

A

Acetate ion, detection, 116–117
  properties, 89
Acidity, regulation of, 35
Alkali group (*see* Cation Group V)
Alkali ions, tests for, 79–81
Aluminum ion, detection, 58
  properties, 45
Aluminum subgroup, analysis, 56–59
  properties, 44
  separation from Iron subgroup, 56–57
Ammonium carbonate group (*see* Cation Group IV)
Ammonium ion, detection, 79
  properties, 76–77
  removal, 63, 77
Ammonium sulfide group (*see* Cation Group III)
Anion Group I, analysis, 112–115
  preliminary experiments, 83–87
  test for, 105, 112
Anion Group II, analysis, 115–117
  preliminary experiments, 88–89
  test for, 105, 115
Anion Group III, analysis, 118–122
  preliminary experiments, 90–95
  test for, 105–106, 118
Anion Group IV, analysis, 123–125
  preliminary experiments, 97–99
  test for, 123
Anion Group V, analysis, 125–127
  preliminary experiments, 99–101
  test for, 106, 125
Anion Group VI, analysis, 127–128
  preliminary experiments, 102
Anion groups, 82
  determination of, 105–106
Anion groups, group reagents, 82
Anions, reactions with acids, 104–105
  systematic analysis of, 102–128
Antimony ion, detection, 42, 43
  properties, 30–31
Antimony tetroxide, analysis, 36
Arsenate ion, analysis, 120–121
  properties, 94–95
  separation from phosphate, 95, 121
Arsenic ions, detection, 40–41
  properties, 29–30
Arsenite ion, detection, 120–121
  properties, 94–95

B

Barium ion, detection, 70–71
  properties, 66
Bismuth ion, detection, 39
  properties, 26–27
Borate ion, detection, 120
  properties, 93–94
Bromide ion, detection, 114
  properties, 83–84
Brown-ring test for nitrate, 97, 123

C

Cadmium ion, detection, 39–40
  properties, 28
Calcium ion, detection, 71
  properties, 68
Carbon, detection in alloys, 133
Carbon dioxide, detection, 92, 119
Carbonate ion, detection, 119
  properties, 91–93

Cation Group I, analysis, 22–23
  preliminary experiments, 15, 19
Cation Group II, analysis, 34–44
  preliminary experiments, 15, 23–32
  separation into subgroups, 36
Cation Group III, analysis, 54–64
  preliminary experiments, 15, 45–52
  separation into subgroups, 44, 56, 57
Cation Group IV, analysis, 69–73
  preliminary experiments, 15, 65–68
Cation Group V, analysis, 78–81
  preliminary experiments, 15, 74–77
Cation groups, group reagents, 14
  separation, 17–18
  tests for, 15
Cations in anion analysis, removal of, 107
  significance of, 106
Centrifuges, 6
Checking in, 11
Chlorate ion, detection, 123–124
  properties, 97–98
Chloride ion, detection, 114
  properties, 83
Chromate ion, detection, 58, 121
  properties, 95
Chromium ions, detection, 58
  properties, 46
Cobalt ion, detection, 39
  properties, 50–51
Complication in Group III by phosphate and oxalate, 54
Copper ion, detection, 39
  properties, 27–28
Copper subgroup, analysis, 37–40
  separation, 36
Cyanide ion, properties, 85

D

Decantation, 5
Delivery tubes, making of, 13
Dichromate ion, detection, 121–122
  properties, 95
    (*See also* Chromate ion)
Digestion, 7
Drop-of-water tests for SiF_4, 100, 125

E

Electromotive series, 140
Elimination of anions, table, 111
Ethyl-acetate test for acetate, 89, 116
Evolution-of-NH_3 test for nitrate, 76, 123

F

Ferric ion (*see* Iron ions)
Ferricyanide ion, detection, 112
  properties, 86
Ferrocyanide ion, detection, 112
  properties, 86
Ferrous ion (*see* Iron ions)
Filtration, methods for, 4–5
Flame tests, 66, 67, 68, 75, 78
Fluoride ion, detection, 125–126
  properties, 99–100
Fluosilicate ion, detection, 125
  properties, 100
Free acids, test for, 103
Fusion procedures, 134–136
  potassium hydrogen sulfate, 134
  sodium carbonate, 135

G

Gas trap for CO_2, 92
Group reagents, for anions, 82, 105–106
  for cations, 14

H

Halide ions, separation by cobalt nitrate, 113

Hydrochloric acid group (*see* Cation Group I)
Hydrogen sulfide, use of, 8–10
Hydrogen sulfide group (*see* Cation Group II)
Hydrogen peroxide test for chromate, 58, 121
Hydroxyl ion, detection, 117
  properties, 89

I

Ignition, 10
Incomplete precipitation, effect of 16
Insoluble salts, analysis of, 133–136
Iodide ion, detection, 114
  properties, 84–85
Iron ions, detection, 60–62
  properties, 49–50
Iron subgroups, analysis, 59–64
  properties, 56–58
  separation from aluminum subgroup, 44, 56

L

Laboratory records, 137–139
Lake tests, 45, 58, 74
Lanthanum nitrate test for acetate, 117
Lead ion, detection, 22, 38
  properties, 19–20, 24–26

M

Macroanalysis, 2
Magnesium ion, detection, 79
  properties, 74–75
Manganese ion, detection, 59–60
  properties, 48
Mercuric ion, detection, 37
  properties, 23–24
Mercurous ion, detection, 22
  properties, 20
Metals and alloys, dissolving of, 131–133
Metaphosphate-bead test for SiO_2, 127
Metastannic acid, analysis of, 36
Microanalysis, 2–3

N

Nickel ion, detection, 61, 70
  properties, 51
Nitrate ion, detection, 123
  properties, 97
Nitrite ion, detection, 116
  properties, 88–89
Non-metallic solids, dissolving of, 133–136

O

Ores, analysis of, 133–136
Organic matter, removal of, 130–131
Oxalate ion, detection, 54
  properties, 93
  removal, 62
Oxide, detection, 117
Oxidizing agents, detection, 104

P

Perchlorate ion, detection, 124
  properties, 98
Periodic table, 152
Permanganate ion, detection, 125
  properties, 48, 99
Pipettes, making of, 13
Phosphate ion, detection, 55, 121
  properties, 94
  removal, 62
  separation from arsenate, 95, 121
Phosphorus, detection in alloys, 132
Potassium hydrogen sulfate fusion, 134
Potassium ion, detection, 80–81
  properties, 75
Prussian blue test, for ferric ion, 50
  for ferrocyanide, 112

R

Reaction, definition, 3
Reagents, list of, 141–146
Records, laboratory, 137–139
Reducing agents, detection, 104
Regulation of acidity, 35
Removal, of ammonium salts, 64, 77
  of phosphate and oxalate ions, 62

S

Semimicroanalysis, 2
Silica, detection, 127–128
  skeleton, test for SiO_2, 102, 127–128
Silicate ion, detection, 127–128
  properties, 102
Silicon, detection in alloys, 133
Silicon tetrafluoride, 100
Silver chloride, decomposition by sodium hydroxide, 83, 114
Silver ion, detection, 22
  properties, 20
Sodium carbonate, decomposition by, 110–112
Sodium carbonate-bead test for silica, 102, 127
Sodium ion, detection, 81
  properties, 75–76
Solids, analysis of, 108–112
Solubility, test for, 108
Solubility tables, 148–151
Soluble group (*see* Cation Group V)
Solute, definition, 3
Solvent, definition, 3
Stannic ion (*see* Tin ions)
Stannic oxide, dissolving of, 36, 135–136
Stannous ion (*see* Tin ions)
Stirring rods, making of, 12
Strontium ion, detection, 71, 72
  properties, 67–68
Sulfate ion, detection, 127
  properties, 100–101
Sulfide ion, detection, 113
  properties, 87
Sulfite ion, detection, 118
  properties, 90–91
Sulfur, free, test for, 113
Systematic analysis, of anions, 102–129
  of general unknowns, 130–136

T

Terms used in chemical analysis, 3–10
Tests, kinds of, 1–2
Thioantimonate ion, properties, 31
Thioarsenate and thioarsenite ions, properties, 30
Thiocyanate ion, detection, 112
  properties, 85
Thiostannate ion, properties, 31
Thiosulfate ion, detection, 118–119
  interference in Anion Group I, 114
  properties, 91
Tin, detection in alloys, 132
Tin ions, detection, 42, 44
  properties, 31–32
Tin subgroup, analysis, 40–44
  properties, 23
  separation from copper subgroup, 36, 41
Turnbull's blue, test for ferricyanide, 112
    for ferrous ion, 50

U

Unknowns, issuance of, 139
  records of, 137–139
Unstable acids, 108–109

W

Wash bottle, preparation of, 11
Washing of precipitates, 7

Z

Zinc ion, detection, 59
  properties, 47